Heterogeneous Chemocatalysis: Catalysis by Chemical Design

Selected papers of Hadi Nur

Editor

Hadi Nur

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Dedication

To my parents,

Nur Anas Djamil
Sofiah Djamaris
The Editor

Dr. Hadi Nur was born in Bukittinggi of West Sumatera in 1969. He received his undergraduate and graduate education in Chemistry and Materials Engineering at Institut Teknologi Bandung (B.Sc. 1992, M.Eng. 1995). Shortly after that he continued his postgraduate studies in Zeolite Chemistry at Universiti Teknologi Malaysia (UTM) (Ph.D. 1998). Postdoctoral studies started with a year as UTM Postdoctoral fellow and two years as Japan Society for Promotion of Science (JSPS) Postdoctoral Fellow at Catalysis Research Center (CRC), Hokkaido University, Sapporo, Japan. He continued stay as Center of Excellence (COE) visiting researcher at CRC for a half year. In May 2002 he joined the Ibnu Sina Institute for Fundamental Science Studies (IIS), Universiti Teknologi Malaysia. Currently he is a lecturer at IIS.
We gave (in the past) knowledge to David and Solomon: and they both said:
“Praise be to Allah, who has favored us above many of His servants who believe”
(an-Naml: 15)

I would like to thank everyone who has, in one way or another, assisted me in the past few years. I am very grateful having for the opportunity to work with very helpful and pleasant collaborates specifically Prof. Dr. Halimaton Hamdan (Universiti Teknologi Malaysia), Prof. Dr. Bunsho Ohtani (Hokkaido University), Assoc. Prof. Dr. Shigeru Ikeda (Osaka University), Assoc. Prof. Dr. Zainab Ramli (Universiti Teknologi Malaysia), Assoc. Prof. Dr. Salasiah Endud (Universiti Teknologi Malaysia) and Assoc. Prof. Mohd Nazlan Mohd Muhid (Universiti Teknologi Malaysia). I would also like to thank the rest of my postgraduate and undergraduate students and my research officers at Universiti Teknologi Malaysia for their support particularly Dr. Didik Prasetyoko, Fitrri Hayati, Eriawan Rismana, Norizah Abdul Rahman, Helda Hamid, Rino Rakhmata Mukti, Ng Yun Hau, Lim Kheng Wei, Gui Lee Kee, Ng Eng Poh, Amir Faizal Naidu Abdul Manan, Izan Izwan Misnon, Chua Yew Hean, Nurulashikin Mohd Ariffin, Shahmeen Ismail, Leiw Sook Fun, Farah Hannah Anuar, Nur Hajarul Aswani Moamail, Sim Sau Teing and Amelia Boon Hoo. The research would not have been possible without financial support from the Japan Society for Promotion of Science (JSPS), Ministry of Science, Technology and Innovation (MOSTI) Malaysia, and The Academy of Sciences for the Developing World (TWAS), Trieste, Italy.
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“No science is created in a vacuum”

Seyyid Hossein Nasr
1 Fundamental: Heterogeneous Chemocatalysis

Introduction

The purpose of this book is to introduce several designs of heterogeneous catalytic systems. The aim is to assist researchers in the field of catalytic chemistry in gaining an understanding of the catalytic phenomena through the design and physicochemical properties of the catalysts. While the book was primarily written for use at the university level, it also may serve as a practical guide for the chemist and chemical engineers.

This is a book of selected papers which I hope will be useful for several purposes. The cohesive aspect of certain advances is shown by bringing together papers published in different journals including, in a few cases, journals of limited circulation. This should aid historical studies. And I hope that it will give to reader a feeling for the general nature of research.

The papers in this book were compiled based on classification from the catalytic processes that contained examples from researches that were made by the editor together with his colleagues and students from 1996 to 2006. I hope that this book can give an inspiration for readers how the design of the catalyst can be related to the physicochemical properties and the catalytic action for the chemical reactions, and may assist in the further search for novel approaches to catalysis. To develop programmable systems and self organizational approaches in chemocatalysis is one of the most challenging design tasks for current catalysis.

What is catalysis?

The name ‘catalysis’ was coined by Berzelius in 1836 [1]. Berzelius defined a catalyst as a substance which by its mere presence evokes chemical actions which would not have taken place in its absence. This definition simply describes the observation of the phenomenon, ‘catalysis’, without making any attempt to interpret or explain its nature. The word was formed from a
combination of two Greek words, κατα (kata) = down and λύειν (lysein) = to split or break. According to Berzelius, by “awaking the affinities which are asleep”, a catalyst breaks down the normal forces which inhibit the reactions of molecules. In another word, a catalyst is a substance that transforms reactants into products, through an uninterrupted and repeated cycle of elementary steps, until the last step in the cycle regenerates the catalyst in its original form. More simply put, a catalyst is a substance that speeds up a chemical reaction without itself being consumed in the process. Many types of materials can serve as catalysts. These include metals, metal compounds (e.g., metal oxides, sulfides, nitrides), organometallic complexes, and enzymes.

**Importance of Catalysis**

It is generally accepted that catalysis plays a fundamental role in the industries. Specifically, two of the largest industry segments, chemicals and petroleum processing, depend on catalysis; many of the modern, cost-and energy-efficient environmental technologies are catalytic; and biocatalysis offers exciting opportunities for producing a broad range of pharmaceuticals and specialty chemicals, and for bioremediation of the environment.

A large fraction of chemical, refinery, and pollution-control processes involve catalysis. Catalysis is critical in the production of 30 of the top 50 commodity chemicals produced in the U.S. and many of the remaining ones are produced from chemical feedstock based on catalytic processes. In broader terms, nearly 90% of all U.S. chemical manufacturing processes involve catalysis [2].

**Heterogeneous chemocatalysis**

Catalysts are classified as *homogeneous* if they are present in the same phase as the reagents. This normally means that catalysts are present as solutes in a liquid reaction mixture. Catalysts are *heterogeneous* if they are present in a different phase. Heterogeneous catalytic reaction systems, in which fluid reactants are passed over solid catalysts, are at present the most widely used catalytic processes in the manufacturing industries.

The selectivity and activity of homogeneous catalysts under mild reaction conditions is unbeaten by their heterogeneous counterparts. Unfortunately, the problem of separating the single-site-catalysts from the reaction media is still an important drawback which blocks large scale applications in industry. Only a few processes are applied nowadays in industry, such as the production of adiponitrile by Dupont, acetic acid by Monsanto and butanal by Celanese (former Ruhr Chemie) [3]. In each case an individual
solution was developed to solve the problem of catalyst separation and recovery. A general toolbox for this has to be filled. In Table 1, the advantages and disadvantages of homogeneous versus heterogeneous catalysis are shown. In this way the major problem of homogeneous catalysis becomes obvious. Solid, heterogeneous catalysts have the advantages of ease of recovery and recycling and readily amenable to continuous processing.

Table 1. Homogeneous versus heterogeneous catalysis.

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<thead>
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<th>Homogeneous</th>
<th>Heterogeneous</th>
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<tr>
<td>Activity</td>
<td>+++</td>
<td>-</td>
</tr>
<tr>
<td>Selectivity</td>
<td>+++</td>
<td>+</td>
</tr>
<tr>
<td>Catalyst Description</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>Catalyst Recycling</td>
<td>-</td>
<td>+++</td>
</tr>
<tr>
<td>Turnover Number</td>
<td>+++</td>
<td>+</td>
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<tr>
<td>Quantity of Catalyst</td>
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Homogeneous catalysis by organometallic complexes [4] is finding wide application in both bulk and fine chemicals and is the method of choice in e.g. carbonylation and hydroformylation. Similarly, biocatalysis [5], which has the advantage of mild reaction conditions and high chemo-, region-, and enantioselectivity, will be increasingly used in fine chemicals manufacture.

The use of microporous solid catalysts such as zeolites and related molecular sieves has an additional benefit in organic synthesis. The highly precise organization and discrimination between molecules by molecular sieves endows them with shape-selective properties [6] reminiscent of enzyme catalysis. The scope of molecular sieve catalysis has been considerably extended by the discovery of ordered mesoporous materials of the M41S type by Mobil scientists [7]. Furthermore, the incorporation of transition metal ions and complexes into molecular sieves extends their catalytic scope to redox reactions and a variety of other transition metal-catalyzed processes [8].

In general, catalyst performance was assessed utilizing appropriate indexes. The most common ones include effectiveness, selectivity, yield, and lifetime. Effectiveness factor relates primarily to the reactant conversion that can be achieved by a certain amount of catalyst, while selectivity and yield relate to the production of the desired species in multiple reaction systems. Much effort has also been invested in the preparation of highly active catalysts. As shown in Table 1, homogeneous catalysis is more active compared to heterogeneous catalysis.
Better catalyst through chemical design

“Catalysis by chemical design” has been a dream for decades. To specify the composition and structure of matter to effect a desired catalytic transformation with desired and predicted rate and selectivity remains a monumental challenge, especially in heterogeneous catalysis. Catalysts operate at a molecular level, so study of their mechanisms falls into the realm of nanotechnology: the science of the extremely small. Most catalytic chemical reactions are heterogeneous – they involve more than one phase. Usually a gas and/or liquid phase passes over a solid catalyst that starts up the reaction – the catalytic converter that cleans up a car’s exhaust gases is a typical example. By contrast, homogeneous catalysis occurs in a single phase, for example the enzyme-modulated reactions that determine the physiology of living organisms.

With the advent of surface science techniques in decades past, the promise was perceived of turning increased molecular level understanding of reaction mechanisms and surface sites into principles of catalyst design. Surface science alone has not proven to be sufficient for this purpose. Over the past decade the rise of powerful, computationally efficient theoretical methods has shown promise, not just for identifying catalytic intermediates and reaction pathways accessible to experiments, but of providing quantitative predictions of energetic for elementary reaction processes not easily accessed experimentally. Much of our work is aimed at the rational design of catalysts for oxidation and acid organic reactions. This chemistry remains one of the most challenging problems in heterogeneous catalysis.

Our principle research interests lie in the fields of synthesis, characterization and catalytic reaction of heterogeneous catalytic system. Based on this principle, our approach may be regarded as an iterative optimisation process, basically consisting of three steps, namely synthesis, characterization and testing as depicted in Figure 1.

The speed at which a progress occurs depends on the quality of the concepts or working hypotheses used to guide this process. Historically, research in catalysis is experimentally oriented, and attempts to make a general organization of information on catalysis would be more of correlation than theory, although the concepts involved in such correlation rest on theoretical grounds. Nowadays, combination of physicochemical inspections of the catalyst characteristic with theoretical chemistry and catalyst modeling is the more effective approach towards understanding how the catalyst was prepared (synthesis), actually ‘looks’ (characterization) and performs (testing). The synthesis of catalyst is divided into three steps: the
the preparation, reaction and isolation. The preparatory step of the catalyst is the most difficult step because many experimental parameters are involved.

In the area of catalysis it is often difficult to establish the mechanism of a reaction through experiment, even though the reactants, products and catalyst are well characterized.

**Classes of catalytic system**

A basic feature common to all catalytic systems is that the catalytic reaction can be considered as a reaction cycle, in which catalytically active sites are initially consumed and at the end of the cycle are regenerated. There are many different catalytic systems. Of most basic mechanistic features are well understood. Here an attempt will be made to classify several catalytic systems which contains example of research works that were carried out by the editor and his colleagues and students. The catalytic systems are the oxidation and acid catalysis by heterogeneous catalysts. I classify our works into four classes:

1. Single center catalyst
2. Hydrophobic-hydrophilic catalytic systems
3. Bifunctional catalyst
4. Synergetic multi reaction center catalyst

The above classification was inspired by classification of catalytic system proposed by Prof. R. van Santen of Technische Universiteit Eindhoven [9]. In
this book, our published papers are divided into four chapters based on the above classification as described in the following chapters.

Chapter 2: Single center catalyst

Catalytic reactions that one could define as belonging to single center catalyst, can be considered as local events. A single metal center or a cluster atoms is required for all of the elementary steps to occur. An example of such a catalytic reaction is dehydration and dehydrogenation of cyclohexanol by aluminophosphate molecular sieves [10-14].

This chapter includes papers on synthesis, characterization and catalytic testing of aluminophosphate molecular sieves. These published papers were based on my PhD work in Department of Chemistry, Universiti Teknologi Malaysia under the supervision of Prof. Halimaton Hamdan. A large part of this works relates to metal-substituted aluminophosphates (MeAPO) molecular sieves. These materials with desired and controllable properties, be adsorptive or catalytic have been successfully synthesized and modified for the specific purposes such as dehydration and dehydrogenation of alcohols reactions. In this research, I substituted Al atom in the framework structure with the divalent metal (Me) atoms (Me = Mn, Mg, Co and Zn) and silicon atom to generate catalytic sites. It is clearly demonstrated that the conversion of cyclohexanol to cyclohexene (as a model reaction) involve the Me–O–P and Si–O–P sites in the framework of AlPO. This result also suggests that MeAPOs are potential catalysts for dehydrogenation of alcohols. It was demonstrated that MnAPSO-5 was the most active catalyst for dehydation and dehydrogenation reactions of alcohols. Based on our understanding on the fundamental factors in the catalytic activity of these materials, results of this research can open the innovation in applied catalysis and play role in industrial catalytic processes. This research was carried out in the period of 1996-1998. This period is an incredibly intense research work. I finally found out what independently doing good science. It was an exhilarating period. I finish my PhD project in two and half years in 1998.

This chapter also includes some papers on single center catalyst published in period of 2002-2006 at Universiti Teknologi Malaysia. The topics of researches include metal complexes encapsulated in Al-MCM-41 as catalysts in oxidation reactions [15-18], enhancement of catalytic activity of TS-1 in epoxidation of 1-octene [19], Ti-OMS-2 as catalyst in oxidation of cyclohexene [20], catalysis by zeolite beta [21,22] and modification of surface of titania by attachment of silica nanoparticle for the enhancement of epoxidation of alkene [23]. The researches were assisted by undergraduate
Chapter 3: Hydrophobic-Hydrophilic catalytic system

One important medium effect that has to be singled out is the hydrophobic-hydrophilic phase interplay possible in the liquid phase. Catalyst systems in which such effects play a role we propose to call hydrophobic-hydrophilic catalytic system [24-34].

In this chapter, a new hydrophobic-hydrophilic catalytic system termed as phase-boundary catalytic system is introduced. The catalyst has been designed in which the external part of the zeolite is hydrophobic, internally it is usually hydrophilic, notwithstanding to polar nature of some reaction centers. In this sense the medium environment in this system is close to that of an enzyme. The major difference between this system and enzyme is accessibility and flexibility. Whereas in this system to a reactant occluded in the micropore many reaction centers are available in enzymes per enzyme cleavage there is usually only one site. Another important difference, as we mentioned before, is lattice flexibility. The lattice of zeolite is rigid, whereas the enzyme is flexible.

Design of hydrophobic-hydrophilic catalytic system

Figure 2 shows schematic representation of design of Phase Boundary Catalytic (PBC) system and its comparison with conventional catalytic system. The PBC is useful primarily for performing reaction at the interface of aqueous phase and organic substrate phases. PBC is needed because the immiscibility of aqueous phase and organic substrate. The name phase-boundary catalysis does what it says; the catalyst acts as a catalyst at the interphase between the aqueous and organic phases as shown in Figure 2. The reaction medium of phase-boundary catalysis system for the catalytic reaction of immiscible aqueous and organic phases consist of three phases; an organic liquid phase, containing most of the substrate, an aqueous liquid phase containing most of the substrate in aqueous phase and the solid catalyst. The two liquid phases are almost completely insoluble in one another.

In case of conventional catalytic system (see Figure 2);

- When the reaction mixture is vigorously stirred, an apparently homogeneous emulsion is obtained, which segregates very rapidly into two liquid phases when the agitation ceases. Segregation occurs by formation of organic bubbles in the emulsion which move downwards to
form the aqueous phase, indicating that emulsion consists of dispersed particles of the aqueous phase in the organic phase.

- Due to the triphasic reactions conditions, the overall reaction between aqueous phase and organic phase substrates on solid catalyst requires different transfer processes. The following steps, which are schematically represented in Figure 3 are involved: 1. transfer of aqueous phase from organic phase to the external surface of solid catalyst; 2. transfer of aqueous phase inside the pore volume of solid catalyst; 3. transfer of the

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**Fig. 2** Schematic representation of the advantage of phase-boundary catalysis in comparison with conventional catalytic system.
substrate from aqueous phase to the interphase between aqueous and organic phases; 4. transfer of the substrate from the interphase to the aqueous phase; 5. mixing and diffusion of the substrate in the aqueous phase; 6. transfer of the substrate from the aqueous phase to the external surface of solid catalyst; 7. transfer of the substrate inside the pore volume of the solid catalyst; and 8. catalytic reaction (adsorption, chemical reaction and desorption).

**Fig. 3** Schematic representation of catalytic action of phase-boundary catalysis in comparison with conventional catalytic system.
It was reported that without vigorous stirring, no reactivity of the catalyst was observed in conventional catalytic system [24-27]. As proposed in Figure 3, it is clear that stirring and mass transfer from organic to aqueous phase and vice-versa are required for conventional catalytic system. In the PBC (see Figure 3), the stirring is not required because the mass transfer is not rate determining step in this catalytic system. It is already demonstrated that this system works for alkene epoxidation without stirring or the addition of a co-solvent to drive liquid-liquid phase transfer [24-27]. The active site located on the external surface of the zeolite particle were dominantly effective for the observed phase boundary catalytic system [27, 29].

The work in this chapter is based on my scientific work in the period of 1999-2002 which was devoted to the development of a novel catalytic system [24-28]. In this period, I worked as Japan Society for Promotion of Science (JSPS) postdoctoral research fellow (1999-2001) and as a Center of Excellent (COE) visiting researcher (2001-2002) in the Prof. Bunsho Ohtani laboratory at Catalysis Research Center, Hokkaido University. I finished my postdoctoral stay which was due to the talented efforts of Dr. Shigeru Ikeda in the Ohtani group. I will always be indebted to Prof. Ohtani for showing me how to do science right. It is a debt that I can never repay, but showing new researchers the joy of chemical research is at least a small effort in this regard not to mention a lot of fun. The research was still continuing after I return to Universiti Teknologi Malaysia in 2002 [29-33].

Chapter 4: Bifunctional catalyst

Another type catalytic systems can be defined as bifunctional. The prototype chemocatalytic system is TS-1 loaded with sulfated zirconia as bifunctional oxidative and acidic catalyst for transformation of 1-octene to 1,2-octanediol [34-37]. The catalyst concerned contains two types of reactive centers, oxidative and acidic. The titanium act as active site for the transformation 1-octene to 1,2-epoxyoctane and the protonic sites hydrolyze the epoxide. The overall reaction consists of two steps, in which an intermediate formed in one reaction olefin is consumed on the other. In heterogeneous catalysis there is usually no control over the sequence of these steps. The control that exists is basically due to differences in the reactivity of the different sites. I gave the idea of this kind catalytic system to Mr. Didik Prasetyoko, a PhD student at Universiti Teknologi Malaysia. His PhD work was supervised by me and Assoc. Prof. Dr. Zainab Ramli and Assoc. Prof. Salasiah Endud. Mr. Didik graduated in 2006.
Chapter 5: Synergetic multi reaction center catalyst

In reactions of synergetic multi reaction center catalyst, at least two different reaction centers that communicate are required. An example is heterogeneous catalyst for liquid-gas reaction system with Mars-van Krevelen type mechanism. A prototype reaction is the oxidation of cyclohexene with molecular oxygen, in the presence of hydrophobic niobium oxide/silica [38].

The oxygen that is inserted into the methylene part of the molecules at a niobium oxide active site is generated from molecular oxygen. The oxygen atom reaches the selective oxidation site via transport through the catalyst.

This chapter contains paper published in the Proceedings of Annual Fundamental Science Seminar 2003, Universiti Teknologi Malaysia [39]. This is only a preliminary study which shows the possibility of synergetic multi reaction center occurred in this catalytic system. Although all the results mentioned above seem consistent with this kind of catalytic action a detail mechanism is still not known.

The following section is the description of the future direction in the field of catalysis which was formulated by Panel on New Directions in Catalytic Science and Technology, National Research Council, the National Academy of Sciences, USA [39] and roadmap for catalysis science in the 21st century written by G. A. Somorjai and K. McCrea [40].

**Future direction in catalytic science and technology**

**New opportunities in catalytic technology** [39]

For viable commercial application, catalysts of any type—heterogeneous, homogeneous, or enzymatic—must exhibit a number of properties, the principal ones being high activity, selectivity, and durability and, in most cases, regenerability. The activity of a catalyst influences the size of the reactor required to achieve a given level of conversion of reactants, as well as the amount of catalyst required. The higher the catalyst activity, the smaller are the reactor size and the inventory of catalyst and, hence, the lower are the capital and operating costs. High catalyst activity can also permit less severe operating conditions (e.g., temperature and pressure), and this too can result in savings in capital and operating costs. The amount of reactant required to produce a unit of product, the properties of the product, and the amount of energy required to separate the desired product from reactants...
and by-products are all governed by catalyst selectivity. As a consequence, catalyst selectivity strongly influences the economics of a process. Catalyst productivity and the time on-stream are dictated by catalyst stability. All catalysts undergo a progressive loss in activity and/or selectivity with time due to chemical poisoning, denaturing, thermal deactivation or decomposition, and physical fouling. When the decrease in performance becomes too severe, the catalyst must be either regenerated or replaced. In view of this, high stability and ease of regeneration become important properties.

Catalysis is a complex, interdisciplinary science. Therefore, progress toward a substantially improved vision of the chemistry and its practical application depends on parallel advances in several fields, most likely including the synthesis of new catalytic materials and understanding the path of catalytic reactions. For this reason, future research strategies should be focused on developing methods with an ability to observe the catalytic reaction steps in situ or at least the catalytic site at atomic resolution. There is also a need to link heterogeneous catalytic phenomena to the broader knowledge base in solutions and in well-defined metal complexes.

Substantial progress and scientific breakthroughs have been made in recent years in several fields, including atomic resolution of metal surfaces, in situ observation of an olefin complexed to zeolite acid sites by nuclear magnetic resonance (NMR) spectroscopy, and in situ characterization of several reaction intermediates by a variety of spectroscopic techniques. Theoretical modeling is now ready for substantial growth as a result of progress in computer technology and in theory itself. For these reasons, it is desirable to focus on areas in which the extensive scientific and technological resources of academe and industry may lead to the fastest practical results. In order of priority, these areas are

1. in situ studies of catalytic reactions;
2. characterization of catalytic sites (of actual catalysts) at atomic resolution (metals, oxides);
3. synthesis of new materials that might serve as catalysts or catalyst supports; and
4. theoretical modeling linked to experimental verification.

Furthermore, additional steps must be taken to facilitate interaction and, in fact, cooperation between industry, dealing with proprietary catalysts, and academe, developing advanced characterization tools for catalysis.

**Roadmap for catalysis science in the 21st century [40]**

In the past, the focus of research in catalysis science was activity to optimize turnover rates. In the future, selectivity to form the desired product without the formation of byproducts will be the major research challenge. Our
understanding of the molecular ingredients of selectivity needs to be improved. New synthetic methods of catalyst preparation are needed for precise control of size, structure, location of additives and location of catalyst particles on supports. Characterization of the catalysts under reaction conditions is essential as the catalyst restructures in the presence of the reactant mixture. Short contact time, high-temperature catalytic processes (catalytic combustion and pyrolysis) are frontier areas of catalysis science. Our concerns with clean air, water and soil provide challenges for catalytic solutions. Global catalytic processes that occur in oceans and in the soil should be explored. The field of enzymatic, heterogeneous and homogeneous catalysis are likely to merge that provide opportunities for developing new catalytic processes.

References

2 Single Center Catalyst

\[ \text{H}_2\text{O} \rightarrow \text{H}^+ + 1/2 \text{O}_2 \]
DEHYDRATION AND DEHYDROGENATION OF CYCLOHEXANOL OVER AIPO₄-5 BASED MOLECULAR SIEVES

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Abstract

The role of incorporated divalent metal (Mn, Mg, Co and Zn) incorporated into the framework of AIPO₄-5 in conversion of cyclohexanol has been examined. The influence of these metals to cyclohexene and cyclohexanone selectivities was correlated to the acidity and basicity properties of these molecular sieves. Possible mechanism for the dehydration and dehydrogenation for cyclohexanol was proposed.

Keywords: AIPO₄-5, acidity, basicity, cyclohexanol

INTRODUCTION

Solids exhibiting acidic and/or base sites on their surfaces play an important role in many catalytic reactions, either as catalysts or supports. Besides their acidic properties AIPO molecular sieves are known to have basic properties [1]. In addition, it was reported that oxygen atoms from the framework may act as basic sites in AIPO molecular sieves [2]. In this study, a series of divalent metal (Me) were incorporated into AIPO₄-5 framework by direct synthesis in order to generate active acid and base sites. The following strategy has been applied to prove the role of active sites in metal-containing AIPO₄-5: Use conversion of cyclohexanol as a representative reaction model [2-4].

The conversion of cyclohexanol was chosen to explain the behavior of both the acid and base sites in AIPO₄-5 molecular sieves by discovering the hidden relationship between acid and base sites.
EXPERIMENTAL

Aluminophosphate (AlPO₄-5) or metal-containing aluminophosphates (MeAPO-5) were synthesized by aluminum isoproxide, Al(OCH(CH₃)₂)₃, as the aluminum source and tripropylamine (Pr₃N) as the template following established procedure with some modifications [1].

MeAPO-5 was synthesized with a gel composition of 1.0 Al₂O₃ : 1.0 P₂O₅ : 0.13 MeO : 40 H₂O Al(OCH(CH₃)₂)₃ (Aldrich) was added to water, the mixture was kept for 12 h (hydrolysis) and was homogenized for 1 h. A separate solution of H₃PO₄ (85% Ajax) with water and Me-acetate (BDH) was prepared and added to the above gel. Then Pr₃N (Aldrich) was added dropwise until the pH ~4.9 was achieved. The gel was heated in a Teflon-lined stainless steel vessel at 175°C for 41 h. The product was washed and dried at 110°C overnight calcined at 550°C in air for 20 h in order to remove the entrapped organic molecules (template). The products were characterized by XRD, SEM, IR, TPD and MAS NMR as described previously [6].

The dehydration and dehydrogenation of cyclohexanol over the samples were carried out using a down-flow, fixed bed, Pyrex reactor of 8 mm internal diameter at atmospheric pressure. The reactor was heated by furnace. Oxygen was then passed through the catalytic bed. The reaction was carried out at 300 °C, with a feed rate of 6 mL h⁻¹ and 0.3 g of catalysts. The reaction mixture was fed from the top using a syringe pump. The water-cooled product was collected at the bottom. The unconverted cyclohexanol and the products were analyzed by a Hewlett Packard Model 5890A gas chromatograph using Flame Ionization Detector (FID). The products were analyzed on Carbowax 20 M column. The column temperature was raised from 35 to 210°C with a rate of 6°C/min.

RESULTS AND DISCUSSION

Figure 1 shows the influence of metal-substituted MeAPO-5 molecular sieves on the selectivity of cyclohexene and cyclohexanone. The overall trend is that selectivity of cyclohexene increases with a decrease in selectivity of cyclohexanone. The detection of cyclohexene indicates the presence of acidic sites, whereas cyclohexanone corresponds to the presence of negative charge on the oxygen atom. As shown in Table 1, the basicity increases with the negative charge on oxygen atom calculated, using Pauling’s third rule [7], increases. Interestingly, it shows that the catalyst with the stronger acid strength exhibits a lower basicity, due to the fact that H⁺ can jump from one oxygen atom to its neighboring oxygen atom. Previously, it was found that the acidity and basicity of MeAPO-5 are structure dependent (T-O-P angle) [6]. Since the calculated trends in Table 1 do not correlate with the experimental data (Fig. 1), quantitatively demonstrates the correlation between the acid strength (at oxygen atom No. 1) with the basic strength (at oxygen atom No. 2) of MeAPO-5.
Fig. 1. Cyclohexanone and cyclohexene selectivities over MeAPO-5

Table 1

Relationship between effective charge of oxygen atom with the acid and base strength of MeAPO-5

<table>
<thead>
<tr>
<th>Me atom</th>
<th>(1) Acid site</th>
<th>(2) Base site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>-2.10</td>
<td>-1.78</td>
</tr>
<tr>
<td>Zn</td>
<td>-2.19</td>
<td>-1.87</td>
</tr>
<tr>
<td>Mn</td>
<td>-2.22</td>
<td>-1.91</td>
</tr>
<tr>
<td>Mg</td>
<td>-2.32</td>
<td>-2.00</td>
</tr>
</tbody>
</table>

- Acid strength increase
- Base strength increase
Fig. 2. Proton transfer in metal substituted aluminophosphate molecular sieves

(a) Dehydration of cyclohexanol

Fig. 3a.
Fig. 3. Proposed mechanisms of (a) dehydration of cyclohexanol over an acid site, and (b) dehydrogenation of cyclohexanol over a base site in AlPO₄-5

According to the scheme shown in Fig. 2, the proton attached to a given oxygen atom of an AlO₄ tetrahedron, (A), can jump to any other oxygen atom belonging to the same tetrahedron (C) via a transition structure (B). This suggests that the protons in AlPO molecular sieves are mobile, which may seem possible from theoretical consideration [8]. The effective charges on those oxygen atoms were calculated in order to explain acidity and basicity properties based on the neighboring oxygen atom. It shows that the stronger acid site is located next to the neighboring atom with a lower basic site.

Dehydration and dehydrogenation of alcohols are catalyzed by the acidic and the base sites, respectively [9]. These reactions provide a diagnostic means of determining the acid-base character of solid surfaces. It is known that
dehydrogenation occurs easily with cyclic alcohols [10]. Alcohols undergo elimination reactions to yield alkenes. Since water is lost in the elimination, this reaction is named dehydration. For secondary alcohols, dehydration follows an E1 mechanism [11], whereby hydroxy group is protonated, a carbocation is formed with loss of a water molecule, followed by the elimination of a proton to yield an alkene. The initial step of acid catalysis by a zeolitic Brønsted acid is proton transfer, where A is AlPO molecular sieve and C is cyclohexanol. This reaction is also known as deprotonation of active sites. The next step of the reaction is the protonation of cyclohexanol, followed by desorption of the base from the active site. Dehydrogenation of cyclohexanol is a proven reaction that can be used to determine base sites in aluminophosphate molecular sieves. Dehydrogenation is a reaction in which hydrogen is eliminated when reacted with oxygen. This is called oxidative dehydrogenation. It has been accepted that the oxidative dehydrogenation involves lattice oxygen ion [12-15]. However, the mechanism of cyclohexanol with acid and base sites in the aluminophosphate molecular sieves is not yet clearly understood. Considering the possible role of acid and base sites in MeAPO-5, the mechanism of dehydration and dehydrogenation of cyclohexanol over these materials are proposed as depicted in Fig. 3.

REFERENCES

The ionic size of metal atoms in correlation with acidity by the conversion of cyclohexanol over MeAPO-5

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(Refereed)

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Abstract

The conversion of cyclohexanol was investigated over MeAPO-5 [Me = Mg, Co, Mn and Zn]. The acidity of the catalysts was correlated with the ionic radii of Me atoms incorporated into the structure of the catalysts. Based on this correlation, it is suggested that the distortion of structure by the larger Me atoms was associated with the T–O–P angle and hence the acid strength. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: A. Microporous materials; D. Catalytic properties

1. Introduction

Crystalline microporous aluminophosphates (AlPO₄-5) [1] contain frameworks of alternating AlO₄⁻ and PO₄⁺ tetrahedra which are electrically neutral; showing no Brönsted acidity. In order to produce Brönsted acidity, an anionic framework has to be generated by substituting an n-valent tetrahedral framework cation, with an (n-1) valent tetrahedral cation. In our previous paper [2], it was shown that the conversion of cyclohexanol is a good pointer to evaluate the Brönsted acidity and basicity of metal-substituted AlPO₄-5 (MeAPO-5). Despite the numerous reports on the correlations between structure and activity of AlPO by theoretical calculations [3–5], experimental evidence of the correlation has never been reported. Furthermore, reports on the incorporation of the various divalent metals into AlPO

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E-mail address: hadi@cat.hokudai.ac.jp (H. Nur).
framework are often varied and inconsistent. Previously, it was demonstrated that metal-substituted AlPO₄-5 is a potential catalyst for dehydration of alcohol [6]. In this work, the conversion of cyclohexanol over MeAPO-5 [Me = Mg, Co, Mn and Zn] was studied in order to correlate the structure, ionic size of Me atoms with acidity of MeAPO-5 by XRD, solid-state ³¹P MAS NMR, XRF and NH₃-TPD.

2. Experimental

AlPO₄-5 and all MeAPO-5 [Me = Mg, Co, Mn and Zn] prepared as described in [1] were characterized after chemical treatment with methanolic HCl in order to remove the template molecules and the extraframework Me [7]. MeAPO-5 was synthesized with a gel composition of 1.0 Al₂O₃:1.0 P₂O₅:0.25 MeO:1.0 Pr₃N:40 H₂O. The samples resulted from the incorporation of manganese, cobalt, zinc and magnesium in the synthesis of AlPO₄-5 are labeled as MnAPO-5, CoAPO-5, ZAPO-5, and MAPO-5 respectively. AlPO₄-5 was used as a reference material for all measurements and calculations discussed hereafter.

The MeAPO-5 samples were characterized by x-ray diffraction (XRD) analysis using Siemens D5000 Diffractometer in the scanning range of 2θ between 2 and 40° using copper Kα (λ = 0.1542 nm at 35 kV and 35 mA) as the source of radiation. Silicon powder was used as an internal standard in the measurement of unit cell parameters in order to correct for any instrumental error which might occur. In all cases the peak at 2θ = 28.4° of silicon (hkl=111) was taken as a reference. Unit cell parameters were calculated from peak position 2θ < 8° in order to minimize errors at low diffraction angle, using the least square refinement techniques. Chemical analysis data were collected by X-ray fluorescence (XRF) analysis using Siemens SRS 303. The MAS NMR experiments were performed using Varian Unity-1 NOVA 400 MHz 9.4T spectrometer. The ³¹P MAS NMR spectra were recorded at 161.87 MHz using 2.0 µs radio frequency pulses, a recycle delay of 1.0 s and a spinning rate of 4.5 kHz. Chemical shifts for ³¹P was referred to 85% H₃PO₄. The samples were characterized after calcination at 400 °C overnight by MAS NMR and XRD.

Ammonia was used as the sorbed molecule in NH₃-TPD experiment. TPD data was acquired from Micromeritics 2900 TPD/TPR. The sample was heated at 500°C for 40 minutes and cooled down to 100°C before passing ammonia. After saturating with NH₃, the sample was flushed with N₂ in order to remove the physically adsorbed NH₃. Temperature for adsorption was increased at a rate of 5°C/min.

The dehydration and dehydrogenation of cyclohexanol over AlPO₄-5 and MeAPO-5 and characterization of their products were carried out as described in [2].

3. Results and discussion

3.1. Physical properties

XRD patterns of AlPO₄-5, MnAPO-5, CoAPO-5, ZAPO-5 and MAPO-5 show that the samples are pure and highly crystalline as reported [6]. The framework of MeAPO-5 by bulk
chemical analysis as tabulated in Table 1 shows a strong evidence of isomorphous substitution of Me atoms by Al into the framework of MeAPO-5. Figure 1 shows the trend in the unit cell parameters of the $a$-axis and $c$-axis of the hexagonal lattice of AFI structure of MeAPO-5 samples respectively. It shows that an increase in parameter $a$ and a decrease in parameter $c$ with the incorporation of divalent metals into the framework. The decrease in parameter $c$ was due to the influence of the size and amount of Me atoms that was incorporated into the framework of AlPO$_4$-5 structure.

Figure 2 shows the relationship between the mean T–O–P angle and ionic radii of metal atom in AlPO$_4$-5 and MeAPO-5 as calculated from the $^{31}$P MAS NMR spectra. The T–O–P angle was calculated using the following relation [8]:

$$\text{mean T–O–P angle/degree} = \frac{(47-\alpha)}{0.51}$$  \hspace{1cm} (1)

where $\alpha$ = chemical shift ppm. It is evident that manganese having the largest ionic radius (0.81Å), imposes the largest effect to the increase of the T–O–P angle, followed by zinc (0.73Å), cobalt (0.72Å), magnesium (0.71Å) and aluminum (0.53Å) respectively. This suggests that the ionic size of the incorporated divalent metal influences the T–O–P angle in the structure of AlPO$_4$-5.

One expects that the higher is the T–O–P angle, the bigger is the unit cell volume. Calculation of the unit cell volume of AlPO$_4$-5 (1384Å), MAPO-5 (1388Å), CoAPO-5 (1387Å), ZAPO-5 (1382Å) and MnAPO-5 (1387Å) show that the unit cell volumes do not follow the trend in the T–O–P because the unit cell volume is not solely affected by the T–O–P angle but by other factors such as the T–O and/or P–O bond lengths, the hydrogen bond and the cation coordination [9,10].

If a large divalent Pb atom (covalent radii = 1.54Å and ionic radii = 1.20Å [11]) is incorporated into the framework of AlPO$_4$-5, the $a$-axis of the unit cell of Pb-AlPO$_4$-5 is smaller than in MeAPO-5 and its $c$-axis is larger than in MeAPO-5. It is calculated from the AlPO$_4$-5 phase that the lattice parameters of Pb-AlPO$_4$-5 are, $a = 13.704$Å and $c = 8.509$Å. Attempt to incorporate a larger atom such as Pb (1.20Å) atom into AlPO$_4$-5 was not successful as pure product could not be obtained. Successful incorporation may be achieved only if the microporous framework is flexible. Referring to the ideal radius ratio for tetrahedral coordination of 0.225–0.414 as suggested by Flanigen et al. [12], the radius ratio for Pb$^{2+}$ is obviously not ideal for tetrahedral coordination in AlPO$_4$-5. This result reinforces our previous observation that the distortion of the structure of MeAPO-5 is caused by the size of the divalent metal atom.

### Table 1
Framework composition of MeAPO-5 and AlPO$_4$-5 by bulk chemical analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Normalized elemental ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Me</td>
</tr>
<tr>
<td>AlPO$_4$-5</td>
<td>-</td>
</tr>
<tr>
<td>MAPO-5</td>
<td>0.03</td>
</tr>
<tr>
<td>MnAPO-5</td>
<td>0.04</td>
</tr>
<tr>
<td>ZAPO-5</td>
<td>0.03</td>
</tr>
<tr>
<td>CoAPO-5</td>
<td>0.03</td>
</tr>
</tbody>
</table>
The result obtained indicates that the incorporation of the Me atoms distorts the structure of MeAPO-5 in the long-range. Short-range order of $^{31}$P in MeAPO-5 suggests that the distortion of MeAPO-5 crystals is correlated with the T–O–P angle.

3.2. Catalytic activity of MeAPO-5

It was observed that cyclohexene and cyclohexanone were the major products in the conversion of cyclohexanol over MeAPO-5. Cyclohexene was the product from the reaction of cyclohexanol in the presence of Brønsted acid sites and cyclohexanone from the reaction of cyclohexanol in the presence of the base sites [2,13,14]. The role of the acid and base sites
and the mechanism of conversion of cyclohexanol over MeAPO-5 has been discussed and reported [2,15]. The percentages of cyclohexene and cyclohexanone are given in Figure 3. The results show the overall trend of the acidity of MeAPO-5 in decreasing order as follows:

MnAPO-5 > ZAPO-5 > CoAPO-5 > MAPO-5  
most acidic  
least acidic

Interestingly, this trend is in agreement with its T–O–P angle (see Figure 2). It is generally accepted that the larger is the T–O–P angle, the stronger is the acid [9,16]. Evidently, in the
The only credible, though complex, relationship between activity and acidity of the MeAPO-5 was found when we considered the acid strength. MnAPO-5, being the strongest acid in the group studied, gave the highest conversion of cyclohexanol and is therefore considered as the most reactive catalyst. However, in our view, acid strength itself is not the only cause of the high activity; the number of acid sites also affects the activity. Counting of acid sites seems to be more difficult. Prior studies have shown that there is a good correlation between the catalytic activity of a solid in certain reaction with the variation in the number of acid centers. The correlation between the amount of ammonia desorbed from the TPD curves with the number of acid sites from the overall composition of MeAPO-5 is shown in Table 2. It shows that the amount of ammonia desorbed among the MeAPO-5 samples is almost the same and is in agreement with the hypothetical concentration of H atom as Brønsted acid. It should be noted that the expected concentrations of the acid sites are estimated from the overall composition. The calculation is based on the assumption that Me atoms occupy the framework position.

The results in Table 2 indicates that the activity of the MeAPO-5 increase in the following order: MnAPO-5 > ZAPO-5 > CoAPO-5 > MAPO-5. Since the ionic radii of Me atom affects the acid strength, it is considered as a measure of activity of the MeAPO-5. The effect of the acid strength of catalyst is clearly observed in Figure 4. From this result, the synergy effect of acid strength and number of acid sites to activity is clearly demonstrated.

The rank of the acidity obtained above contradicts the result observed by Pozas et al. [17]. They observed that the dehydration of ethanol increases over catalysts in the following order CoAPO-5 > ZAPO-5 > MnAPO-5. Calculation of lattice parameter by Pozas et al. shows that the incorporation of Mn, Co and Zn into AlPO₄-5 implies a lattice expansion compared to the original AlPO₄-5. However, they observed that the cell parameters of the hexagonal lattice of AFI structure type of CoAPO-5, ZAPO-5 and MnAPO-5 are similar. Our observations are different because the distortion of MeAPO-5
follow the trend of the ionic radii of Mn, Co and Zn. The Me concentration used by us in the synthesis of MeAPO-5 differs from those used by Pozas et al. Elemental ratio of Me reported by Pozas et al. was 0.010–0.014. Instead we increased the Me content threefold. Clearly these changes influence the distortion of the hexagonal lattice of the AFI structure.

A possible explanation for the difference between our results and that of Pozas et al. is that, the incorporation of a large amount of Me atom into the framework of AlPO$_4$-5 not only cause distortion of the hexagonal lattice of the AFI structure, but also demonstrates the effect of ionic radii of Me atom on the structure. This effect was not clearly observed for a lower concentration of Me atom. The order of activity for MeAPO-5 with the lower concentration of Me atom was in agreement with the effective charge on oxygen atom calculated using Pauling’s third rule as reported earlier [2].

4. Conclusions

The correlation between the ionic radii of divalent metals incorporated into the framework with the acidity of MeAPO-5 catalysts was observed in the conversion of cyclohexanol. The acidity of catalysts was correlated with the ionic size of Me atom in MeAPO-5 according to the following order: Mn$>$Zn$>$Co$>$Mg. The metal-substituted AlPO$_4$-5 influences the acid strength and number of acid sites. The number of acid sites is the controlling factor in cyclohexanol conversion. Both structural (T–O–P angle) and chemical formula are factors that affect the acidity of MeAPO-5.

References


Probing the active sites of aluminated mesoporous molecular sieve MCM–41 by secondary synthesis in the conversion of cyclohexanol

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The active sites of H-Al-MCM-41 aluminated by secondary synthesis have been probed by the conversion of cyclohexanol and compared with those of H-Al-MCM-41 prepared by direct synthesis, purely siliceous MCM-41, AlPO₄-5 and H-ZSM-5. Conversion of cyclohexanol produces cyclohexene, cyclohexanone and 3-methylpentane in the presence of Brønsted, basic and Lewis acid sites respectively. Whereas cyclohexanol is converted to polyaromatic compounds in the presence of very strong acid sites as those found in H-ZSM-5. The formation of cyclohexene as the only product of conversion over H-Al-MCM-41 prepared by direct and secondary synthesis indicates the presence of Brønsted acid sites in both systems, which is not observed in the purely siliceous MCM-41 and AlPO₄-5 samples. The larger amount of cyclohexene formed over H-Al-MCM-41 by secondary synthesis suggests that there is a higher degree of Brønsted acidity in this system than that of H-Al-MCM-41 by direct synthesis. However, the strength of acidity in H-Al-MCM-41 by secondary synthesis is weaker than that of H-ZSM-5. In addition, the results of this reaction, supported by IR spectroscopy study, do not indicate the presence of Lewis acidity in H-Al-MCM-41 prepared by secondary synthesis.

1. INTRODUCTION

Mesoporous molecular sieve MCM-41 attracts much attention because of its unique properties \cite{1, 2} and potential as catalysts in reactions involving large organic molecules \cite{3-6}. Purely siliceous MCM-41 does not show significant catalytic activity as it lacks the ion exchange capability due to its electrically neutral framework. However, the isomorphous substitution of the framework Si by aluminium or other trivalent cations offers a mechanism for generating acidity and for modifying the chemical properties of the purely siliceous MCM-41. The incorporation of aluminium into the framework of MCM-41 is particularly important as it gives rise to Brønsted acid sites. It has been reported that
calcined Al-MCM-41 has acid properties similar to those of amorphous silica [7]. However, it has not been firmly established whether the acidity is due to the Brønsted acidic protons which are ion-exchanged in order to balance the necessary number of framework negative charges introduced by the incorporation of aluminium, or attributed to the formation of extraneous framework aluminium which are associated with the presence of Lewis acidity.

In a recent communication [8], we have succeeded in preparing mesoporous aluminosilicate MCM-41 materials by isomorphous substitution via secondary synthesis. The success of preparing Al-MCM-41 by such a technique offers great advantages in tailoring Al-MCM-41 as catalyst with variable acidic properties for specific reactions. Therefore, it is of interest to identify and understand the nature of active sites present in these materials; whether it is acidic, basic or cationic. In previous acidity studies [9,10], pyridine or ammonia adsorption is most often used to determine the concentration and strength of the Brønsted and Lewis acid sites in zeolitic materials. In our study presented here, the cyclohexanol conversion has been chosen as the probe reaction.

In the conversion of cyclohexanol, two reactions can occur: the dehydration into cyclohexene and water and the dehydrogenation leading to cyclohexanone. The dehydration of cyclohexanol occurs due to the presence of Brønsted acid sites, whereas the dehydrogenation of cyclohexanol takes place in the presence of surface basic sites (Figure 1). Therefore besides identifying the nature of active sites, it is possible to estimate the relative acidity of H-AlMCM-41 prepared by both direct and secondary synthesis based on this diagnostic test reaction. In addition, the catalytic behaviour of these materials in cyclohexanol conversion is compared with other catalysts: AlPO₄-5 that possesses some weak basic sites and H-ZSM-5, which is strongly acidic and has been shown to be an excellent catalyst for the conversion of alcohol to gasoline [11,12].

![Figure 1. Schematic representation of the dehydrogenation of cyclohexanol to cyclohexene and the dehydration of cyclohexanol to cyclohexene.](image-url)
2. EXPERIMENTAL

Sample of H-ZSM-5 was supplied by N. E. Chenocat, Japan and AlPO₄-5 molecular sieve was synthesized as described elsewhere [13]. The synthesis, treatment and characterization of purely siliceous MCM-41 and aluminosilicate MCM-41 (Si/Al = 2.8, 3.6 and 3.8) is made according to the procedure described previously [8]. Calcined Al-MCM-41 sample (Si/Al ≈ 3.8), is used for the protonic ion exchange procedure performed with 1 M NH₄NO₃ solution at 90 °C (with liquid-to-solid ratio of 50 ml/g). H-Al-MCM-41 was obtained by deammoniating the ammonium form of Al-MCM-41 at 550 °C in air. Sample of Al-MCM-41 by direct synthesis was prepared according to a literature method [2]. The cyclohexanol conversion reaction was performed over 0.5 g of H-Al-MCM-41, H-ZSM-5 (Si/Al ratio ≈ 38), AlPO₄-5 and purely siliceous MCM-41 using a continuous flow, fixed bed microreactor at 400 °C and atmospheric pressure, with a feed rate of 0.05 ml/min. Cyclohexanol was a BDH product with 99% purity and used as received. Product distribution was determined by a Shimadzu GC-14B gas chromatograph equipped with an FID detector and a 50 m fused silica capillary column with helium as carrier gas. The products were identified on the basis of their mass spectra using Hewlett Packard 5890 Series II gas chromatograph and Hewlett Packard 5982A mass spectrometer. For IR studies on MCM-41 materials, thin self supporting wafers of about 10 mg/cm² were prepared and activated in situ in the IR cell fitted with CaF₂ windows at 400 °C in vacuum for 16 h. The infrared spectra were recorded in the range of 4000–1300 cm⁻¹ using a Perkin Elmer 1600 spectrometer with a resolution of 2 cm⁻¹.

3. RESULTS AND DISCUSSION

The infrared spectra of hydroxyl groups of the purely siliceous MCM-41 and secondary aluminated MCM-41 are shown in Figure 2(i) in the region of stretching vibrations of O-H bands. A very intense band at 3744 cm⁻¹ was observed in the IR spectrum of the parent MCM-41 corresponding to terminal silanol groups. These groups have been previously observed on amorphous silica and microporous zeolites and reported to reveal a very weak acid character [14]. The IR results clearly show that the MCM-41 samples have very large amount of silanol groups, the largest population being in the purely siliceous MCM-41.

It is seen that incorporation of aluminium in the purely siliceous MCM-41 samples leads to a decrease in the intensity of the IR band assigned to terminal Si-OH hydroxyls (3744 cm⁻¹) which is shifted to 3742 cm⁻¹. This is presumably connected with structural redistributions resulting from the insertion of Al species into the mesoporous structure during aluminisation. After adsorption of pyridine at room temperature, the OH stretch band at 3742 cm⁻¹ shows a loss in intensity and broadens as seen in Figure 2(ii), due to the interaction with the pyridine molecules, indicating the presence of weak acid sites.
Figure 2. FTIR spectra of the hydroxy groups of (i) activated MCM-41 samples and (ii) after pyridine adsorption.

Figure 3(i) depicts the spectrum of pyridine chemisorbed on the purely siliceous MCM-41, showing no Brønsted acidity and a weak Lewis acidity. The same IR bands due to pyridinium ions and to pyridine bonded to Lewis sites but of lower intensities were observed with the desorption of pyridine at higher temperatures. Secondary aluminated MCM-41 of various concentrations exhibit two IR bands associated with Brønsted acidity (B) at 1540 cm⁻¹ and Lewis acidity (L) at 1450 cm⁻¹ respectively as shown in Figures 3(ii)–(iv). It is observed that the amount of Brønsted acidity increases as the amount of aluminium in the framework of secondary Al-MCM-41 increases. The ratio of observed intensity of the Brønsted band, $I_B$, to the Lewis band, $I_L$, for Al-MCM-41 with the Si/Al = 2.8 is $I_B/I_L = 2.3$. The formation of a small amount of strong Lewis acid sites, i.e. octahedrally coordinated Al species in the aluminosilicate sample may be affiliated with the presence of octahedral Al in the MCM-41 framework [15]. We note that these acid sites are rather strong in Al-MCM-41 as pyridine is still present on the sample after outgassing at 400 °C. Moreover, when the experiment was performed with purely siliceous MCM-41, the peaks hardly persist upon evacuation of the sample at 250 °C. That was an additional evidence that strong Lewis acid sites were generated upon substitution of framework Si⁺⁺ by Al⁺⁺.
Figure 3. FT-IR spectra of adsorbed pyridine on (i) purely siliceous MCM-41 and Al-MCM-41 samples with (ii) Si/Al = 2.8, (iii) Si/Al = 3.6 and (iv) Si/Al = 3.8 evacuated at a = 25 °C, b = 250 °C and c = 400 °C.
Table 1 shows the values of total conversion of cyclohexanol to cyclohexene at 400°C over H-Al-MCM-41, Si-MCM-41, AlPO₄-5 and H-ZSM-5. The results show that at 400 °C cyclohexanol conversion is the highest over secondary aluminated H-Al-MCM-41 which produces cyclohexene as the only product at nearly 100 % conversion. This confirms that secondary aluminated H-Al-MCM-41 consists only of Brønsted acid sites. H-Al-MCM-41 prepared by direct synthesis yielded a lower rate of dehydration of cyclohexanol, suggesting a lower concentration of Brønsted acid sites in this system, confirming the poor incorporation of aluminium in the framework. As expected, the purely siliceous MCM-41 did not show any catalytic activity towards the conversion of cyclohexanol to cyclohexene due to the absence of Brønsted acidity. This material has been characterized to have mainly Lewis acidity by means of IR spectroscopy using pyridine adsorption. The only product detected from the test reaction is 3-methylpentane. In contrast, cyclohexanol was converted to cyclohexene and cyclohexanone in the presence of AlPO₄-5. The formation of cyclohexanone in this reaction indicates that some basic sites are also present in AlPO₄-5, as already reported by other workers [16,17]. In the case of H-ZSM-5, cyclohexanol is mostly converted to cyclohexene with a small amount of polycyclic compounds as minor products confirming its well-known acidic nature. In this context, H-Al-MCM-41 prepared by secondary synthesis is less acidic as compared to H-ZSM-5, which inhibits consecutive disproportionation and isomerization reactions of cyclohexene.

4. CONCLUSIONS

Secondary aluminated Al-MCM-41 contains weak Brønsted acid sites that are not present in the purely siliceous sample. The concentration of the Brønsted acid sites increases with the amount of aluminium inserted into the

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion wt. [%]</th>
<th>other products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cyclohexene</td>
<td>cyclohexanone</td>
</tr>
<tr>
<td>H-Al-MCM-41 (secondary)</td>
<td>100</td>
<td>none</td>
</tr>
<tr>
<td>H-Al-MCM-41 (direct)</td>
<td>83</td>
<td>none</td>
</tr>
<tr>
<td>Si-MCM-41</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>98</td>
<td>none</td>
</tr>
<tr>
<td>AlPO₄-5</td>
<td>78</td>
<td>22</td>
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</tbody>
</table>
MCM-41 framework. Catalytic conversion of cyclohexanol to cyclohexene result demonstrates that H-Al-MCM-41 prepared by secondary synthesis contains only Brönsted acid sites with a higher concentration than the one present in the directly synthesized H-Al-MCM-41. The Al-MCM-41 materials in this study is hydrothermally stable and is a potential catalyst in acid-catalyzed conversion of alcohols at moderate temperatures.

REFERENCES

Deactivation Modes and Reactions of HZSM-5, AIPO₄-5 and MnAPSO-5 in the Conversion of Cyclohexanol

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Abstract—Conversion of cyclohexanol has been used to investigate the deactivation modes of the HZSM-5, AIPO₄-5 and MnAPSO-5. Conversion of cyclohexanol as a test reaction was used to evaluate the activity of these catalysts.

Abstrak—Penukaran siklohksanol telah digunakan untuk mengkaji cara nyahaktif HZSM-5, AIPO₄-5 dan MnAPSO-5. Penukaran siklohksanol sebagai tindak balas uji telah digunakan untuk menilai keaktifan mangkin tersebut.

In our previous work [1, 2], it was found that the conversion of cyclohexanol is a good pointer to evaluate the Brønsted acidity from dehydration of cyclohexanol to cyclohexene and basicity from dehydrogenation of cyclohexanol to cyclohexanone of HZSM-5 and metal-substituted AIPO₄-5. It was demonstrated that manganese-silicon-substituted AIPO₄-5 (MnAPSO-5) was a potential catalyst for dehydration of alcohol [3]. In this work, the possible reaction of coke formation on HZSM-5 and MnAPSO-5 during the conversion of cyclohexanol is presented. The formation of coke in these catalysts was analysed by TGA, IR and GC-MS.

A more general definition of coke proposed by Karge [4] consists of carbonaceous deposits which is deficient in hydrogen compared with the coke-forming reactant molecules. In this study, we have chosen the definition proposed by Guisnet and Magnoux [5]: Coke is a carbonaceous compounds (polyaromatic or nonpoly-aromatic) formed during a reaction which is responsible for deactivation.

In this work, the activity, stability and lifetime of MnAPSO-5 in the conversion of cyclohexanol were also studied.

Experimental

Dehydration and Dehydrogenation of Cyclohexanol

HZSM-5 was supplied by N. E. Chemcat
Single Center Catalyst

Deactivation Modes and Reactions of HZSM-5, AlPO₄-5 and MnAPSO-5 in the Conversion of Cyclohexanol

Corporation, Japan. MAS-NMR analysis shows that the Si/Al ratio is 38. The AlPO₄-5 and MnAPSO-5 were prepared using the procedure given in [3]. All samples were calcined at 550°C for 20 hours in air before the reaction. Cyclohexanol (Riedel-de Haën) was used as purchased. The dehydration and dehydrogenation of cyclohexanol over the samples were carried out using a down flow, fixed bed, Pyrex reactor of 8 mm internal diameter at atmospheric pressure. The reactor was heated by a furnace. Oxygen was then passed through the catalytic bed. The reaction was carried out at 300°C, with a feed rate of 0.1 mL/min and 0.3 g of catalyst. The reaction mixture was fed from the top using a syringe pump. The water-cooled product was collected at the bottom. The unconverted cyclohexanol and the products were analysed by a Hewlett Packard Model 5890A gas chromatograph using Flame Ionisation Detector (FID). The products were analysed on Carbowax 20 M column. The column temperature was raised from 35°C to 210°C with a flow rate of 6°C/min. The activity of catalyst is expressed in terms of conversion (amount of transformed reactant per amount of inlet reactant) and selectivity (amount of desired product per amount of converted reactant).

For the optimisation of dehydrogenation of cyclohexanol, the MnAPSO-5 was used as the catalyst. The reaction was carried out in the temperature range of 100–400°C, with a feed rate of 0.05 mL/min and the amount of catalysts of 0.3 g.

Characterisation of Coke in HZSM-5 and MnAPSO-5

Differential thermogravimetry analysis (DTG) was performed in air using a Mettler TG50 with a scan rate of 10°C/min. GC-MS analysis was carried out using Hewlett Packard 5890 Series II gas chromatograph and Hewlett Packard 59827A mass spectrometer.

Results and Discussion

As expected, AlPO₄-5 did not show any catalytic activity due to the absence of Bronsted acidity. Cyclohexanol was converted to cyclohexene and cyclohexanone in the presence of MnAPSO-5 catalyst. Analysis of the products of cyclohexanol conversion over HZSM-5 by GC-MS indicated that cyclohexene was the major product followed by a light molecule (m/e = 58–58) and some aromatic compounds as the minor products (Figure 1).

Thermogravimetric analysis of HZSM-5 indicates two distinct weight losses as shown in Figure 2. Two temperature ranges representing the weight changes to two processes are observed: 100–250°C which corresponds to the removal of 'zeolitic' water, and 350–650°C which is typical of elimination of the coking products. In contrast, no significant peak is observed in DTG curve of AlPO₄-5 and MnAPSO-5 samples after reaction, indicating that no coke was formed in these samples.

The composition of coke depends on four parameters [6]: (i) reaction conditions, (ii) nature of reactants and/or intermediates and/or products, (iii) pore structures and (iv) active sites. If parameters (i) and (ii) are assumed constant, two important aspects related to deactivation of HZSM-5 and AlPO₄-5 based molecular sieves are delineated namely, pore structure and active sites. Pore structure and active sites are the main factors thought to determine the deactivation of a microporous material in a catalytic reaction. It is difficult to evaluate with precision the effect of the pore structure on the formation of coke since it is impossible to obtain the same acidity for molecular sieves of different pore structure [5, 7, 8]. However, it is obvious that the formation of coke is generally greater when there is more space available for its formation (e.g. in the cavities or at the channel intersection) and the intermediates to coke formation diffuse.
more slowly into the gas phase [5]. If we look into the pore and channel network of HZSM-5 and AlPO₄-5 based molecular sieves in more detail, it is observed that the HZSM-5 consists of interconnecting channels and AlPO₄-5 has non-interconnecting channel network (see Figure 3). From this point of view, it is suggested that the channel in AlPO₄-5 molecular sieves are more likely to be blocked by coke formation rather than HZSM-5. However, the accessible cages in HZSM-5 are much larger than in AlPO₄. As a result, the transition state for formation of coke is more easily formed in HZSM-5 than in AlPO₄. Furthermore, note that the size of apertures of the framework structures for HZSM-5 and AlPO₄ are different. The size of aperture of HZSM-5 is 0.54 x 0.56 Å and for AlPO₄-5s is 7.3 Å. It was found that the most strongly acidic sites as found in HZSM-5 lead to detrimental irreversible adsorption, coking, and deactivation of catalyst [9].

The acidic sites in HZSM-5 are strong at high temperatures. Being a superacid, it is capable of protonating paraffins and thereby initiating catalytic cracking [10]. Gates [10] described that catalytic cracking involves many complicated side reactions which disturbs the formation of carbenium ions. These ions decompose to give hydrogen and carbenium ions, which may deprotonate and undergo isomerisation,
Deactivation Modes and Reactions of HZSM-5, AIPO₄-5 and MnAPSO-5 in the Conversion of Cyclohexanol

Figure 2. The TG and DTG patterns of HZSM-5 after cyclohexanol conversion.

Figure 3. Types of pore channel networks in zeolites.

disproportionation and alkylation. As shown in Figure 4, from GC-MS analysis, many complicated products may be formed. HZSM-5, having smaller pores, are proved to be blocked than the larger pores in AIPO₄.

As stated above, zeolites exhibit a high catalytic activity for the formation of coke over the temperature range of 300–600°C. The mechanism of coke formation is rather complex and involves several reaction steps. It is generally accepted that coke formation over acidic solids is derived from extensive dehydrogenation of fused ring aromatics [4, 11, 12]. Experimentally, if we check the type of coke that is formed using IR, we arrived at different conclusions. IR spectroscopy was one of the first techniques employed to investigate the nature of carbonaceous deposits laid down
Figure 4. The minor products (< 3%) of conversion of cyclohexanol over HZSM-5 determined by GC-MS.

on zeolite catalysts during hydrocarbon reactions [4, 13]. Figure 5 shows the IR spectra of HZSM-5 before and after the conversion of cyclohexanol. It shows that the IR bands of saturated hydrocarbons (ν = 2939 cm⁻¹ and 2864 cm⁻¹) appear in the spectra. However, CH bands at wavenumbers higher than 3000 cm⁻¹, which indicate the presence of aromatics, were not observed. These peaks did not appear in the MnAPSO-5, suggesting that the coke is mainly paraffinic. However, the coke also contains a small amount of polyaromatic compound that is not detectable by IR. In HZSM-5 dissolved in 40% hydrofluoric acid, a small insoluble coke in the form of black particle was observed. Its black colour, indicates that its components are polyaromatic [5]. Guisnet and Magnoux [5] described that the soluble coke molecules are the intermediate in the formation of insoluble coke. They proposed that (i) insoluble coke is not formed at low coke content and (ii) the aromativity of the soluble coke increases with the coke content (indeed insoluble coke is composed of highly polyaromatic molecules).

Dehydration of cyclohexanol over MnAPSO-5

In our previous papers [1, 2], it has been demonstrated that MnAPSO-5 is the best catalyst for dehydration and dehydro-
Deactivation Modes and Reactions of HZSM-5, AlPO₄-5 and MnAPSO-5 in the Conversion of Cyclohexanol

genation of cyclohexanol compared to the other metal-substituted AlPO₄-5. Since MnAPSO-5 only generates a weak basicity, it only produces a small amount of cyclohexanone as the product of dehydration of cyclohexanol. Because of that, dehydration of cyclohexanol was chosen in order to investigate the activity, regenerability and lifetime of the catalyst.

Figure 6 shows that conversion of cyclohexanol at 100°C was not observed. Knowing that the boiling point of cyclohexanol is 181°C; at 100°C the reaction was expected to take place in the liquid phase. This means that the activity of the catalyst for this reaction depends on whether the reactant exists as a gas phase or a liquid phase. It shows that the MnAPSO-5 was active at a temperature higher than the boiling point of cyclohexanol. In addition, the viscosity of reactant also affects the degree of conversion, since a viscous liquid is difficult to diffuse through unidimensional channel of AlPOs. Figure 7 shows that the viscosity decreases when the temperature increases [14].

As shown in Figure 8, the conversion of cyclohexanol decreased from 78% to 7% after 10 hours. After this period the catalyst was activated at 550°C for 4 hours in order to remove the species or coke which could possibly block the active sites. The catalyst was used again and the result indicated that the activity was increased to 75%. After repeating the process for three times, the catalyst was still active, suggesting that its structure did not collapse during reaction and upon heat treatment.

**Conclusions**

It is concluded that the type of coke formed in the channel of HZSM-5 after conversion of cyclohexanol is paraffinic. The sites on the outer zeolitic surface contribute to the production of polyaromatic hydrocarbon which was also considered for coke.
formation of HZSM-5. The size of the polyaromatic hydrocarbon is larger than the pore size of HZSM-5 and is considered being the cause of the pore blocking on the outer zeolitic surface as shown in Figure 9. The coke molecules located on the outer surface of the crystallites can block the access to the sites of channel intersection where there are no coke molecules. The formation of polyaromatic in the channel of HZSM-5 is prevented by steric constrains in HZSM-5. The results of the cyclohexanol reaction over HZSM-5 are summarized in Figure 9. Step 1 is not "demanding" and is accelerated by the presence of acid centers of different nature and strength. Step 2 and 3 occur only on strong acid sites. Cyclohexanol conversion was terminated at step 1 over MnAPSO-5.

Temperature is an important factor which influences the conversion of cyclohexanol over MnAPSO-5 catalyst. The conversion of cyclohexanol takes place above the boiling point of cyclohexanol (> 161°C).

References


Structural distortion in MeAPO–5 molecular sieves: a $^{31}P$ MAS-NMR study

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ABSTRACT: Solid-state magic-angle spinning (MAS) nuclear magnetic resonance (NMR) was used for characterization of a series of metal containing microporous aluminophosphate of AFI type (MeAPO–5 with Me: Mg, Co, Zn and Mn). The position of Me atoms, whether in the framework or extraframework have been examined using $^{31}P$ MAS NMR and bulk chemical analysis. It was found that $^{31}P$ chemical shift values carried information about the distortion of MeAPO–5 structures by Me atoms which was correlated to the ionic size of Me atoms incorporated into their framework.

KEYWORDS: Microporous materials; Nuclear resonance
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1 INTRODUCTION

Crystalline microporous aluminophosphates of AFI type (AlPO$_4$–5) is a large pore molecular sieve consisting of a unidirectional, 12-ring channel system [1,2]. AlPO$_4$–5 contains frameworks of alternating AlO$_2$– and PO$_2$+ tetrahedra which are electrically neutral; showing no Brønsted acidity. In order to produce Brønsted acidity, an anionic framework has to be generated by substituting an n-valent tetrahedral framework cation, with an $(n-1)$ valent tetrahedral cation. In AlPO$_4$–5, this can be done either by replacing the pentavalent phosphorus with Si, or by replacing the trivalent aluminium with a divalent ion. This class of materials is potentially important acid catalyst materials [3]. Although the influence of divalent metal atoms to the catalytic properties of MeAPO–5 (Me: Mg, Co, Zn and Mn) was reported [4], it has been experimentally difficult to verify that the transition metal ion (Me) incorporated by hydrothermal synthesis is actually in the framework. These heteroatom-substituted AlPO are very difficult to characterize because of the variety of possible locations, coordinations and oxidation state of the metals ions. Despite several characterization techniques used, important questions still remain which include the following: Are the metals incorporated into tetrahedral framework positions? What is the effect of incorporated metal atoms to the local structure? What is the maximum loading of metal ions? Although no single methods is available to answer all these questions up to know, in this paper we demonstrated that these questions could be answered only by interpretation of $^{31}P$ MAS NMR spectra and chemical analysis of a series of MeAPO–5.

2 EXPERIMENTAL

The synthesis of divalent metal substituted AlPO$_4$–5 are described in [1]. MeAPO–5 was synthesized with a gel composition of 1.0 Al2O3:1.0 P2O5:0.25 MeO:1.0 Pr3N4:40 H2O. The samples resulted from the incorporation of manganese, cobalt, zinc and magnesium in the synthesis of AlPO$_4$–5 are labeled as MnAPO–5, CoAPO–5, ZAPO–5 and ZAPO–5 respectively. AlPO$_4$–5 was used as a reference material for all measurements and calculations discussed hereafter. The MAS NMR experiments were performed using Bruker Avance 400 MHz 9.4T spectrometer. The $^{31}P$ MAS NMR spectra were recorded at 161.87 MHz using 0.5 ms radio frequency pulses, a recycle delay of 1.0 s and spinning rate of 7.0 kHz. Chemical shifts for $^{31}P$ was referred to 85% $H_3PO_4$. The MeAPO–5 samples were characterized by x-ray diffraction (XRD) analysis using Bruker D8 Diffractometer in the scanning range of 2θ between 2 and 40° using copper $K\alpha$ ($\theta = 0.1542$ nm at 35 kV and 35 mA) as the source of radiation. Silicon powder was
used as an internal standard in the measurement of unit cell parameters in order to correct for any instrumental error which might occur. In all cases the peak at 2θ = 28.4° of silicon (Kα1 = 111) was taken as a reference. Unit cell parameters were calculated from peak position 2θ > 8° in order to minimize errors at low diffraction angle, using the least square refinement techniques. Chemical analysis data were collected by X-ray fluorescence (XRF) analysis using Siemens SRS 303.

3 RESULTS AND DISCUSSIONS

The $^{31}$P MAS NMR spectra of AlPO$_4$–5 and MeAPO–5 are shown in Fig. 1. Generally the spectra are broad with the main peak centred around -30 ppm corresponding to P(4Al) tetrahedra and shoulders around -24 ppm and -22 ppm assigned to P(Me, 3Al) and P(2Me, Al) respectively. Detail assignments of signals in each sample are given in Tab. 1. Comparatively, the distribution of peaks varies for each sample. The results of the deconvolution of MAPO–5 and ZAPO–5 $^{31}$P are presented in Tab. 1.

$^{31}$P is a spin I = 1/2 nucleus (with no quadrupole moment), and $^{31}$P MAS NMR can distinguish between different environment. However, spectral signals are broadened by the presence of transition metals. The degree of broadening of the spectral signals due to the presence of Mg$^{2+}$ and Zn$^{2+}$ are expected to be less than Mn$^{2+}$ and Co$^{2+}$ in MeAPO–5. Due to the fact that Mn$^{2+}$ and Co$^{2+}$ are paramagnetic, their unpaired electron(s) can produce very efficient relaxation of the neighbouring nucleus and cause broadening of the spectral signals [5]. Mn$^{2+}$ and Co$^{2+}$ occur in high abundance and possess high magnetogyric ratios. Because of that, the resolution of the signals of the Mn- and Co-containing AlPO$_4$–5 are lower, hindering the elucidation of their $^{31}$P MAS NMR spectra. In addition, the broadening of the $^{31}$P MAS NMR peak of MnAPO–5 can be correlated with the distortion of the structure. This is explained by the influence of the size (ionic radii) of Me atom; a larger Me atom distorts the structure of MeAPO–5. The structure of MnAPO–5 is more distorted than CoAPO–5 because the ionic radius of Mn$^{2+}$ (0.80 Å) is larger than Co$^{2+}$ (0.72 Å).

As shown in Fig. 1, the $^{31}$P chemical shift around -30 ppm assigned to the P(4Al) environment for MeAPO–5 is different. The shift is due to the increase in T-O-P (T : Me or Al) bond angle of the framework [6]. The average T-O-P angle around the P(4Al) tetrahedral site was calculated based on the
Single Center Catalyst

**Figure 1:** $^{31}P$ MAS NMR spectra of $AlPO_4$–5 and $MeAPO$–5 (ppm from $H_3PO_4$): (a) $AlPO_4$–5, (b) $MAPO$–5, (c) $CoAPO$–5, (d) $ZAPO$–5, (e) $MnAPO$–5.

**Figure 2:** Relationship between mean T-O-P angle and ionic radii of metal atom in $AlPO_4$–5 and $MeAPO$–5.

Empirical correlation [6]. The dependence of the $^{31}P$ chemical shift on the T-O-P angle is according to the relation:

$$\text{mean } T - O - P \text{ angle/degree} = \frac{47 - \alpha}{0.51},$$

(1)

where $\alpha$ is chemical shifts ppm.

Fig. 2 shows the relationship between the mean T-O-P angle and the ionic radii of metal atom in $AlPO_4$–5 and $MeAPO$–5. The atom with the largest ionic radii showing the largest mean T-O-P angle is Mn and the lowest ionic radii size showing the lowest angle is Al. Calculation of the unit cell of $MeAPO$–5 using their XRD patterns showed that manganese having the largest ionic radius (0.81) imposes the largest effect to the increase of the T-O-P angle, followed by zinc (0.73), cobalt (0.72), magnesium (0.71) and aluminum (0.53) respectively. This suggests that the ionic size of the incorporated divalent metal influences the T-O-P angle in the structure of $AlPO_4$–5. One expects that the higher is the T-O-P angle, the bigger is the unit cell volume. Calculation of the unit cell volume of $AlPO_4$–5 (1384, $MAPO$–5 (1388), $CoAPO$–5 (1387), $ZAPO$–5 (1382) and $MnAPO$–5 (1387) show that the unit cell volumes do not follow the trend in the T-O-P because the unit cell volume is not solely affected by the T-O-P angle but by other factors such as the T-O and/or P-O bond lengths, the hydrogen bond and the cation coordination [7,8]. The result obtained, indicates that the incorporation of the Me atoms distorts the structure of $MeAPO$–5 in the long-range. Short-range order of $^{31}P$ in $MeAPO$–5 suggests that the distortion of $MeAPO$–5 crystals is correlated with the T-O-P angle.

Although the relationship between $^{31}P$ chemical shift with T-O-P angle is only based on the empirical evidence, several authors have attempted to create a unified theoretical foundation for $^{31}P$ chemical shift in all classes of phosphorus compounds [69-14], but success here depends on the fact that we are dealing with only limited structural variation. The other influencing factor on the $^{31}P$ chemical shift is that, the extraframework divalent metal molecules causes further distortion to the tetrahedral $P$ which corresponds to $P(Al)l$ site. The presence of the larger extraframework divalent metal molecules may cause steric strain on the T-O-P ($T$: Me or Al) bond angle. In order to release the strain and accommodate the larger extraframework Me molecules, the bond angle has to be readjusted. To exclude this possibility, the extraframework divalent metals were removed by treatment with methanolic HCl [15]. It was observed that no significant difference in the chemical shifts and linewidth of $^{31}P$ MAS NMR peaks between $AlPO$s.
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treated with methanolic HCl compared to those as synthesized. This proves that the distortion of T-O-P angle is not caused by the extraframework divalent metals. From this result, it can be suggested that the size of the incorporated divalent metal can change the T-O-P angle in the AlPO₄-5 based materials structure.

The following relationship was used to estimate the quantity of divalent metals in the framework position from the ³¹P MAS NMR which is assigned to $P(4Al)$ sites [16]:

$$M_e = \frac{\sum_{n=0}^{4}(4-n)I(P_{nAl})}{\sum_{n=0}^{4} I(P_{nAl})}.$$  (2)

The observation of the peak area in the spectrum relates to the amount of phosphorus atom in these samples. Tab. 2 shows the percentage of substitution of Me for Al in the samples; calculated by deconvolution of NMR peaks. The results show little agreement with the chemical analysis results. This implies that some portion of Me occupy the extraframework position in the samples. This result is in agreement with result reported by Blasco et al. for Mg-containing AFI aluminophosphates [17].

4 CONCLUSIONS

³¹P MAS NMR spectra of AlPO₄-5 and MeAPO-5 prove that their corresponding framework structure is distorted by the incorporation of divalent metal. It is shown that the T-O-P (T: Mn, Zn, Co and Mg) angle is different from that of Al-O-P angle from AlPO₄-5. Calculation of the amount of incorporated divalent metals is only possible for MAPO-5, and ZAPO-5 because broadening of signal occurs in the presence of Mn and Co in MnAPO-5, and CoAPO-5. Although deconvolution of ³¹P MAS NMR spectra shows that incorporation of divalent metal occurs, by comparison with the chemical analysis data, it shows that a portion of the divalent metals also occupy the extraframework position.

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Modification of titanium surface species of titania by attachment of silica nanoparticles

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Abstract

Silica nanoparticles-attached titania ($\text{TiO}_2@\text{SiO}_2$) was prepared by modification of the surface of titania ($\text{TiO}_2$) with octadecyltrichlosilane (OTS) as a source of silica. The attachment of silica was achieved through repeated deposition–hydrolysis–calcination of OTS on the surface of titania particles. For comparison, the silica–titania composite ($\text{TiO}_2–\text{SiO}_2$) containing titania and silica agglomerated particles was also prepared. The physicochemical characteristics of $\text{TiO}_2@\text{SiO}_2$ and $\text{TiO}_2–\text{SiO}_2$ particles are experimentally studied by X-ray diffraction (XRD), UV–vis diffuse reflectance (UV–vis DR), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX) and $^{29}\text{Si}$ solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) techniques. The effect of silica attaching on activity of titanium surface species has been tested in the liquid phase epoxidation of 1-octene to 1,2-epoxyoctane with aqueous hydrogen peroxide. It is demonstrated that the surface attachment of titania with silica nanoparticles enhances the epoxidation activity of titania. UV–vis DR spectra of the solid particles showed the increase in intensity of the tetrahedral titanium in $\text{TiO}_2@\text{SiO}_2$. This indicates the occurrence of the transformation of some of the octahedral titanium to the tetrahedral structure during silica attaching of $\text{TiO}_2@\text{SiO}_2$ in which titanium tends to bond with $-\text{Si(OH)}_2(\text{OSi})_2$ to make it stable in tetrahedral form. Considering that the tetrahedral titanium was considered the most active species in epoxidation of alkenes, it can be concluded that a high epoxidation activity of $\text{TiO}_2@\text{SiO}_2$ particle was related to the modification of the local environment of titanium surface species by attachment of silica nanoparticles.

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Keywords: Silica nanoparticles-attached titania; Titanium surface species; Surface modification

1. Introduction

Titanium dioxide or titania is one of the most utilized particulate materials in the world. Although it was discovered more than 200 years ago and has been commercially processed for 85 years, it is still being actively researched. Titania is the most widely used as pigment in cosmetic and paint products, and photocatalyst. The photochemical activity of titania is modified by promoting or suppressing the recombination of electron and hole pairs which are formed by UV light excitation [1]. High photochemical activity is required when titania is used as photocatalyst, whereas low photochemical activity is preferred for paint or cosmetics application. One of methods to improve the photocatalytic activity of titania is by attachment of silica. It has been reported that the photocactivity of silica-incorporated titania was three times higher than that of the Degussa P25 [2]. However, the reason why the photocactivity of silica-incorporated titania gave a higher activity compared to that of bare titania have not yet been clearly understood.

Recently room temperature sol–gel attachments of silica have been successfully adopted in order to coat titania with silica [3]. The attachment of titania with stable oxide layers has been also done by spraying of a metal oxide precursor solution on the surface of titania nanoparticles [4–6], acid hydrolysis of polysilicate [7] and hydrolysis of tetraethylorthosilicate (TEOS) using chloroform catalyst [8]. However, attachment of silica on the surface of titania by using octadecytrichlorosilane (OTS) as a source of silica had not been investigated yet. OTS was selected because it is well-known compound used in surface-modification reactions with surface hydroxyl groups.

Recently, Park and Kang [9] also successfully prepared silica-coated titanium dioxide by using TEOS as a source of silica. In such system, silica is evenly coated on the surface of...
titania with thickness in the range of 10–15 nm. However, in this study, the strategy is different from those previously reported [2–9] because the aim is not to cover titania with silica but to attach silica nanoparticles on the surface of titania. One expects that the local environment of titanium surface species of titania are modified by attachment of silica. Evenly-coated silica on the surface of titania could not be achieved by using this method, since the presence of long chain alkyl groups (C18) of OTS hinder the formation of silica layer during the surface modification. To examine the activity Ti surface species, the epoxidation of 1-octene by using aqueous H2O2 was used as the probe reaction.

In contrast to well-documented techniques to attach the silica on the surface of titania, to date, there is very limited understanding on the correlation between preparation and the nature of the titanium surface species after attachment of silica. It has been generally accepted that functional attachment of silica on the surface of titania must be controllable, reproducible and tailored surface structures. The tailoring of the surface properties is especially important for functional attachment. In this paper, attachment of titania particles with silica nanoparticles involves a simple deposition–hydrolysis–calcination of OTS on the surface of titania particles. It is demonstrated that the attachment of silica provides the modification of the local environment of titanium surface species of titania.

2. Experimental

2.1. Preparation of silica nanoparticles-attached titania

Silica nanoparticles-attached titania catalyst was prepared by modification of the surface of anatase TiO2 (Riedel-de Haën) with octadecyltrichlorosilane (OTS) (Sigma–Aldrich) as a source of silica. The TiO2 powder (6 g) was immersed in toluene (20 ml) containing OTS (3000 μmol) and the suspension was stirred for 20 min at room temperature. The suspension was centrifuged to remove unreacted OTS and wash with toluene (60 ml) and precipitated were dried at 383 K overnight. Then, the sample was ground to obtain a fine powder. In the next step, the sample was calcined at 550 °C for 4 h. Now, the silica-attached titania was achieved through deposition–hydrolysis–calcination processes. All the steps were repeated nine times, starting from the beginning until the accumulation of silica on the surface of titania was achieved. The silica-attached titania obtained was labeled as TiO2@SiO2. A similar procedure was also carried out to prepare the titania–silica composite (TiO2–SiO2) without

![Fig. 1. IR spectra of (a) TiO2, (b) TiO2@SiO2, and (c) TiO2–SiO2.](image1)

![Fig. 2. X-Ray diffractograms pattern of (a) TiO2, (b) TiO2@SiO2, and (c) TiO2–SiO2.](image2)

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Atomic percentage of silicon and titanium of TiO2, TiO2@SiO2, and TiO2–SiO2*</th>
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<td>Element</td>
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<td>91.3</td>
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<td>TiO2–SiO2</td>
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* Chemical analysis using energy dispersive X-ray analysis (EDAX).
washing with toluene in the above procedure for preparation of TiO$_2$@SiO$_2$. In a typical experiment, OTS (3000 μmol) was dissolved in toluene (20 ml). A dried titania powder (6 g) was added to the solution and the mixture was stirred in the fume cupboard until the solvent was completely dry. Then, the sample was ground to obtain a fine powder and calcined at 550 °C for 4 h.

2.2. Characterizations

The TiO$_2$, TiO$_2$@SiO$_2$ and TiO$_2$–SiO$_2$ were characterized by UV–vis diffuse reflectance (UV–vis DR), X-ray diffraction (XRD), Fourier transform infrared (FTIR), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX) and $^{29}$Si solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) techniques. UV–vis spectra were recorded using Perkin-Elmer Lambda 900 spectrometer. XRD patterns were acquired on a Bruker D8 Advance instrument using Cu Kα radiation ($λ$ = 1.5418 Å, kV = 40, mA = 40). SEM photographs and elemental analysis of silica and titanium elements in the solid particles were obtained by using Philips XL 40 instrument. The $^{29}$Si MAS NMR experiments were performed using Bruker Avance 400 MHz 9.4T spectrometer. The spectra were recorded at 79.44 MHz using 4 μs radio frequency pulses, a recycle delay of 60 s and spinning rate of 7.0 kHz using a 4 mm zirconia sample rotor. $^{29}$Si MAS NMR chemical shifts were referred to external TMS at 0 ppm.

2.3. Activity of Ti surface species

To examine the activity Ti surface species, the epoxidation of 1-octene by using aqueous H$_2$O$_2$ was used as the probe reaction. It is generally known that silica is not active in this reaction [10–12]. In the epoxidation reaction, 1-octene (4 ml, Aldrich), 30% aqueous H$_2$O$_2$ (1 ml) and solid powder (50 mg) were placed in a glass tube, and the reaction was performed with stirring for 24 h at ambient temperature. The resulting product were withdrawn and analyzed with gas chromatograph (GC). Gas chromatograph–mass spectrometer (GC–MS) was also used to verify the resulting product.
3. Results and discussion

3.1. Physical properties

Fig. 1 shows the FTIR spectra of TiO$_2$, TiO$_2$@SiO$_2$ and TiO$_2$–SiO$_2$ particles, respectively. The peaks at 678 and 505 cm$^{-1}$ are attributed to Ti–O bond and the peak at 678 cm$^{-1}$ refers to symmetric O–Ti–O stretch while 505 cm$^{-1}$ is due to the vibration of Ti–O bond. A new distinct and strong peak at 1081 cm$^{-1}$ can be observed in TiO$_2$@SiO$_2$ which assigned to the asymmetric Si–O–Si stretching vibration indicating the presence of silica in the TiO$_2$@SiO$_2$. The band of silica at 1075 cm$^{-1}$ can be observed in TiO$_2$–SiO$_2$ but it is less intense compared to the peak of silica of TiO$_2$@SiO$_2$. An absorption peak of Ti–O–Si was observed at 950 cm$^{-1}$ in TiO$_2$@SiO$_2$ particles indicating the Ti–O–Si bond formation [9]. The C–H peaks were not observed in the FTIR spectra of TiO$_2$@SiO$_2$ and TiO$_2$–SiO$_2$ due to alkyl groups of OTS have been removed after calcinations.

Table 1 shows the percentage of Ti and Si in TiO$_2$, TiO$_2$@SiO$_2$ and TiO$_2$–SiO$_2$ samples. The atomic percentage of Si in TiO$_2$, TiO$_2$@SiO$_2$ and TiO$_2$–SiO$_2$ are 0.0%, 8.7% and 2.5%, respectively. Fig. 2 shows the XRD pattern of TiO$_2$, TiO$_2$@SiO$_2$ and TiO$_2$–SiO$_2$. The major peaks appear at 25.4$^\circ$ corresponds to the monoclinic phase of titania anatase. The X-ray diffractograms show that TiO$_2$@SiO$_2$ and TiO$_2$–SiO$_2$ possess a similar XRD pattern with bare titania indicating the anatase structure of titania remain unchange after the attachment of silica. As shown in Fig. 2, a broad hump with maxima at about 12$^\circ$ which is attributed to amorphous silica is clearly observed in TiO$_2$–SiO$_2$ diffractogram. However, there is no a broad hump about 12$^\circ$ can be observed for TiO$_2$@SiO$_2$ although the amount of silica in TiO$_2$@SiO$_2$ is higher than that of TiO$_2$–SiO$_2$ (see Table 1). This phenomenon was also observed in the FTIR spectra of TiO$_2$@SiO$_2$ and TiO$_2$–SiO$_2$. The band of silica at 1075 cm$^{-1}$ can be found in TiO$_2$–SiO$_2$ but it is less intense compared to the silica peak of TiO$_2$@SiO$_2$ (see Fig. 1). This suggests that the silica particles attached on the surface of TiO$_2$ in TiO$_2$@SiO$_2$ is very well dispersed with very small crystallite size which cannot be observed by XRD. This observation was supported by SEM photographs shown in Fig. 3.

Fig. 3 shows the SEM photographs of TiO$_2$, TiO$_2$@SiO$_2$ and TiO$_2$–SiO$_2$. It reveals the difference in surface morphology among the samples. It is clearly observed the existence of silica nanoparticles, with the size in the range of 20–50 nm, attached on the surface of TiO$_2$@SiO$_2$. However, TiO$_2$ and SiO$_2$ particles are very difficult to distinguish in TiO$_2$–SiO$_2$ since their size and shape are almost similar.

UV–vis DR spectra of TiO$_2$, TiO$_2$@SiO$_2$ and TiO$_2$–SiO$_2$ are shown in Fig. 4. As shown in spectra, the band in the range of 230–280 nm is attributed to a charge transfer of the tetrahedral titanium sites between O$^{2-}$ and the central Ti (IV) atom, while octahedral Ti was reported appear at around 260–330 nm [13,14]. It shows that the increase in intensity in the range of 230–280 nm indicates the occurrence of the transformation of some of the octahedral titanium framework to the tetrahedral structure during the attachment of silica.

The short-range order structure of the TiO$_2$@SiO$_2$ and TiO$_2$–SiO$_2$ was characterized by $^{29}$Si MAS NMR measurements (see Fig. 5). As a measure of cross-linkage, the ratio of Q$^4$ to Q$^3$ sites are attributed to the degree of cross-linking. It has been calculated that the ratio Q$^4$ to Q$^3$ sites of TiO$_2$@SiO$_2$
and TiO$_2$–SiO$_2$ is almost similar (ca. 1.7). $Q$ denotes the presence of the corresponding Si sites in the spectra: $Q^4 = \text{Si(OH)OSi}^4$, $Q^3 = \text{SiOH(OSi)}^3$, and $Q^2 = \text{Si(OH)OSi}^2$. Interestingly, as shown in Fig. 5, attachment of silica on the surface of TiO$_2$ in TiO$_2$@SiO$_2$ led to the formation of $Q^2$ site. However, the amount of $Q^2$ type of bonding is only ca. 6% due to a partial condensation of $Q^2$ to $Q^3$ and $Q^4$ sites during repeated deposition–hydrolysis–calcination of octadecltrichlorosilane (OTS) processes. Based on the above results, it is suggested that the deposition–hydrolysis–calcination of OTS to produce silica nanoparticles led to the formation of $\text{Si(OH)OSi}^2$ bonding in the sample, although this type bonding is considerably a little amount in TiO$_2$@SiO$_2$.

3.2. Activity of Ti surface species

As can be seen in Fig. 6, all of solid particles showed activity for epoxidation of 1-octene to give 1,2-epoxyoctane. In particular, attachment of silica nanoparticles (TiO$_2$@SiO$_2$) led to better activity than TiO$_2$–SiO$_2$ composite. This phenomenon could be explained in terms of the local environment of Ti active site. As described previously, the difference in the UV–vis DR spectra of TiO$_2$, TiO$_2$–SiO$_2$ and TiO$_2$@SiO$_2$ samples is due mainly to coordination of titanium on the surface of titania. It is generally accepted that isolated Ti (IV) in tetrahedral form are considered the most active species in epoxidation reaction [10–12]. Based on these facts, the effect of attachment of silica on increasing the epoxidation activity of TiO$_2$@SiO$_2$ can be explained by the presence of isolated Ti (IV) in tetrahedral form. However, the apparent rate of epoxidation over TiO$_2$@SiO$_2$ was much lower than those previously reported [16]. One of the reasons for the low epoxidation activity in TiO$_2$@SiO$_2$ particles is the presence of few four-coordinate Ti species which are considered to be the most active species in olefin epoxidation [17]. On the basis of these results, a model of the titanium surface species after attachment of silica nanoparticles is proposed (see Fig. 7). One considers that titanium tends to bond with $\text{Si(OH)OSi}^2$ to make it stable in tetrahedral form.

4. Conclusions

The silica nanoparticles have been successfully attached on the surface of titania by deposition–hydrolysis–calcination of octadecltrichlorosilane (OTS). It is demonstrated that the surface attachment of titania with silica nanoparticles enhances the epoxidation activity of titania. UV–vis DR spectra of the solid particles showed the increase in intensity of the tetrahedral titanium in TiO$_2$@SiO$_2$. This indicates the occurrence of the transformation of some of the octahedral titanium to the tetrahedral structure during silica attaching of TiO$_2$@SiO$_2$ in which titanium tends to bond with $\text{Si(OH)OSi}^2$ to make it stable in tetrahedral form. Considering that the tetrahedral titanium was considered the most active species in epoxidation of alkene, it can be concluded that a high epoxidation activity of TiO$_2$@SiO$_2$ particle was related to the modification of the local environment of titanium surface species by attachment of silica nanoparticles.

Acknowledgments

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References

Sulphated AlMCM-41: Mesoporous solid Brønsted acid catalyst for dibenzoylation of biphenyl

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Abstract

Sulphated mesoporous solid Brønsted acid catalyst (SO₄-AlMCM-41) was prepared by impregnation of sulphuric acid on the surface of H-AlMCM-41. Characterization of SO₄-AlMCM-41 by pyridine adsorption studies and ²⁷Al MAS NMR showed that the presence of Brønsted acidity was correlated with octahedrally coordinated aluminium and solvent environment. Catalytic study demonstrated that the SO₄-AlMCM-41 catalyst has a higher activity in the dibenzoylation of biphenyl with benzoyl chloride than sulphuric acid, H-AlMCM-41 and sulphated amorphous silica.

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Keywords: Sulphated AlMCM-41; Brønsted acidity; Dibenzoylation; Biphenyl

1. Introduction

Benzoylation is an important Friedel-Crafts acylation used in the commercial production of important chemicals such as benzophenone and its substituted analogues as additives in the synthesis of fine chemicals and dyes [1–5]. Recent interest is on the dibenzoylation of biphenyl with benzoyl chloride, from which the monosubstituted product, 4-phenyl-benzophenone or 4-benzoylbiphenyl (4-PBP), a useful precursor in perfumes, and the disubstituted product, 4,4'-dibenzoylbiphenyl (4,4'-DBBP), an important monomer in the polymerisation of poly(4, 4'-diphenylene diphenylenevinylene) or namely PDPV are formed [6–8].

Current production of disubstituted 4,4'-DBBP is still via the difficult homogeneously catalysed process [6]. Despite the increase of research activities in the field of heterogeneous catalysis, synthesis of disubstituted compound using zeolite has not so far been successful. Although heterogeneously catalysed reactions using microporous molecular sieve did not show much potential, the large internal surface area and channel apertures of mesoporous molecular sieve MCM-41 is a promising alternative for reactions involving large molecules. Purely siliceous MCM-41 materials have no substantial acidity, and so there is continuing interest in the incorporation of metal or non-metal in order to create acid sites. Besides, the presence of Brønsted and Lewis acid sites in H-AlMCM-41 play significant roles in enhancement of the catalytic activity and adsorptive capacity [9–11].

The first example of successful formation of disubstituted 4,4'-DBBP catalysed by mesoporous H-AlMCM-41 with 100% selectivity was reported; however, with very low conversion (0.05%) [9–10]. Recently, a number of studies on sulphation of AlMCM-41, in order to increase the acidity, have been reported [12–16]. However, they demonstrated that the sulphated AlMCM-41 only exhibits Lewis acidity.

In this work, we present a simple preparation method to generate solid Brønsted acid catalyst by introducing sulphate groups onto the surface of AlMCM-41. The catalytic activity of the sulphated AlMCM-41 was studied in the dibenzoylation of biphenyl with benzoyl chloride reaction. The results obtained over sulphated AlMCM-41 were compared with those obtained using sulphuric acid, H-AlMCM-41 and sulphated amorphous silica.

2. Experimental

2.1. Synthesis of AlMCM-41

The AICM-41 with SiO₂/Al₂O₃ of 15 was synthesized according to established procedure [9]. Sodium silicate was prepared by dissolving 6.13 g of rice husk ash (97% SiO₂) and
2.00 g of NaOH in 40 ml distilled water at 80 °C for 2 h under stirring. The resulting solution was labelled as solution A. Another solution (solution B) was prepared by mixing 0.7558 g of NaAlO₂ (Riedel-de-Haën®, 50–56% Al₂O₃), 6.07 g of CTABr and 0.70 g of NH₄OH 25 wt.% in 35 ml distilled water, followed by stirring at 80 °C until a clear solution was obtained. Both solutions A and B were mixed together in a polypropylene bottle to give a gel with a composition of 6 SiO₂:CTABr:1.5 Na₂O:0.15 (NH₄)₂O:250 H₂O, followed by vigorous stirring. The resulting gel was kept in an air oven for crystallization at 100 °C for 24 h. The gel was then cooled to room temperature and the pH of the gel was adjusted close to 10.2 by adding 25 wt.% acetic acid. The heating and pH adjustment was repeated twice. The solid product was calcined at 550 °C in air for 3 h. Finally, the solid product was washed with deionized water and dried at 110 °C. The ion-exchange was repeated three times. H-AlMCM-41 was then calcined at 550 °C. Sulphation of H-AlMCM-41 was carried out by adding H₂SO₄ (95–98%) in a round bottom flask. The mixture was stirred at 80 °C until a clear solution was obtained.

2.2. Preparation of H-AlMCM-41 and sulphated AlMCM-41

H-AlMCM-41 mesoporous material was prepared by ion-exchange of 0.70 g cal-AlMCM-41 sample with 50 ml of 0.2 M NH₄NO₃ at 60 °C for 6 h. The solid was filtered, washed with deionized water and dried at 110 °C for 2 h. The ion-exchange was repeated three times. H-AlMCM-41 was then calcined at 550 °C. Sulphation of H-AlMCM-41 was carried out by adding H₂SO₄ (0.50 g) to 10 ml toluene and 30 μl H₂SO₄ (95–97%) in a round bottom flask. The mixture was stirred at 50 °C for 1.5 h and dried at 130 °C for 12 h. The sulphated AlMCM-41 is labelled as SO₄-AlMCM-41.

2.3. Characterization of the mesoporous materials

MCM-41 mesoporous materials were characterized by powder X-ray Diffraction (XRD) using a Bruker Advance D8 using Siemens 5000 diffractometer with Cu Kα radiation (λ = 1.5418 Å, 40 kV, 40 mA). Infrared spectra were acquired by using a Perkin Elmer Spectrum One FT-IR spectrometer with a 4 cm⁻¹ resolution and 10 scans in the mid IR region (400–4000 cm⁻¹). 27Al MAS NMR spectra were recorded using a Bruker Ultrashield 400 spectrometer at a frequency of 104.2 MHz with a spin rate of 7 kHz, pulse length of 1.9 ms, and relaxation time delay of 2 s and 6000 scans. The chemical shifts of 27Al were reported in relation to Al(H₂O)₆³⁺. TG-DTA measurements were carried out on a Perkin Elmer’s Pyris Diamond Thermogravimetric/Differential Thermal Analyzer under nitrogen atmosphere with a flow rate of 20 ml min⁻¹ for 10 mg sample. Samples were heated in the temperature range of 45–850 °C with a heating rate of 10 °C min⁻¹. The specific surface area was analyzed by using the multi-point BET technique with a surface area analyzer instrument (Thermo Finnigan Qsurf Series). Pyridine FTIR spectra were recorded using a Bruker Spectra One FT-IR spectrometer.

Fig. 1. X-ray diffraction patterns of (a) uncal-AlMCM-41; (b) cal-AlMCM-41; (c) H-AlMCM-41; and (d) SO₄-AlMCM-41.
H-AlMCM-41, implying highly ordered structures. As a consequence of template removal upon calcination, the intensity of the (1 0 0) peak increases and shifts to a lower d-value, indicating more ordered framework structure and a decrease in the unit cell parameters, respectively.

It is also observed that the structural order of MCM-41 material changes after treatment with NH$_4$NO$_3$ and H$_2$SO$_4$. After ion-exchange with NH$_4$NO$_3$, there is a decrease in intensity of the (1 0 0) peak of H-AlMCM-41, indicating a decrease in the order of the mesoporous structure. Comparatively, the intensity of peaks in the XRD pattern for SO$_4$-AlMCM-41 (Fig. 1(d)) is further reduced and broadened, suggesting either a partial loss of structural order or possible decrease in the particle size of the sulphated MCM-41 material. As indicated by the surface properties data shown in Table 1, there is not much change in the unit cell parameters of the sample upon sulphation. However, there is a marked decrease in pore volume and surface area of the SO$_4$-AlMCM-41 sample relative to the H-AlMCM-41 sample. This strongly suggests that sulphate groups have been successfully immobilized in the pore of MCM-41.

The infrared spectra of the uncal-AlMCM-41, cal-AlMCM-41, H-AlMCM-41 and SO$_4$-AlMCM-41 molecular sieves are presented in Fig. 2(a)–(d), respectively. The broad peak around 3420 cm$^{-1}$ is due to O–H stretching of water; the bands at around 2924 and 2854 cm$^{-1}$ shown in Fig. 2(a) are assigned to symmetric and asymmetric stretching modes of the C–H sp$^3$ groups of the organic template. The corresponding bending mode of C–H is observed at 1480 cm$^{-1}$. The peak at around 1640 cm$^{-1}$ corresponds to bending mode of O–H. The peaks around 1229 and 1084 cm$^{-1}$ are attributed to the asymmetric stretching of Si–O–Si groups. The symmetric stretching modes of Si–O–Si groups are observed at around 799 and 578 cm$^{-1}$. The peak at 965 cm$^{-1}$ is assigned to the presence of defective Si–OH groups, while the adsorption band at 455 cm$^{-1}$ corresponds to the bending vibration of Si–O–Si or Al–O–Si groups. Fig. 2(b) also shows that the symmetric and asymmetric modes of the C–H sp$^3$ group of the template are absent in the spectra of calcined samples, indicating that the organic template has been removed successfully. The IR spectrum of SO$_4$-AlMCM-41 material in Fig. 2(d) shows a few additional peaks. The additional band at 1288 cm$^{-1}$ corresponds to the stretching vibration of the S–O bond, and the absorption band at 1179 cm$^{-1}$ is due to symmetric vibrations of Si–O–S bridges. In addition, the band observed at 884 cm$^{-1}$ is assigned to symmetric S–O stretching vibrations, whereas the band at 806 cm$^{-1}$ is assigned to symmetric Si–O stretching mode. The SO$_4$ deformation frequency has been assigned in the region 580 cm$^{-1}$ [12,17]. Thus, all these results indicate that the sulphuric acid has been successfully anchored on the walls of AlMCM-41.

The TG profile of the uncal-AlMCM-41, H-AlMCM-41 and SO$_4$-AlMCM-41 samples are depicted in Fig. 3. Basically, the TG of uncal-AlMCM-41 sample follows a three-stage weight loss profile, with the first stage occurring below 200 °C, the second stage between 200 and 400 °C, and the third stage above 400 °C. The first stage is attributed to the removal of physically adsorbed water, while the second stage is associated with the removal of the organic template.

Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>d-spacing (Å)</th>
<th>$a_0$ (Å)</th>
<th>Surface area (m$^2$ g$^{-1}$)</th>
<th>Pore volume (cm$^3$ g$^{-1}$)</th>
<th>Acidity$^a$ (μmol g$^{-1}$)</th>
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<tr>
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<td>44.07</td>
<td>50.88</td>
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<td>–</td>
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<tr>
<td>Cal-AlMCM-41</td>
<td>39.81</td>
<td>45.97</td>
<td>–</td>
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<tr>
<td>H-AlMCM-41</td>
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<td>44.06</td>
<td>1079</td>
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<td>19.8</td>
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<tr>
<td>SO$_4$-AlMCM-41</td>
<td>37.89</td>
<td>43.75</td>
<td>549</td>
<td>0.28</td>
<td>112.9</td>
</tr>
</tbody>
</table>

$^a$ Acidity of samples was measured at 250 °C.

Fig. 2. Infrared spectrum of (a) uncal-AlMCM-41; (b) cal-AlMCM-41; (c) H-AlMCM-41; and (d) SO$_4$-AlMCM-41.

Fig. 3. Thermogravimetric analysis of (a) H-AlMCM-41; (b) SO$_4$-AlMCM-41; and (c) uncal-AlMCM-41 samples in nitrogen gas with 20 °C/min heating rate.
loss. The first stage loss (around 5%) was due to desorption of water and adsorption of gas molecules (<200 °C). In the second stage, a high-temperature weight loss peak (~33%) at 200–450 °C was also observed, which corresponds to the decomposition of template in the samples via Hofmann elimination. The third stage weight loss (~3%) was due to water produced by thermal condensation of silanol groups to siloxane groups (450–550 °C) [18]. Meanwhile, SO₄-AlMCM-41 shows two additional and distinct weight losses, at 200–300 and 300–600 °C, due to the decomposition of sulphate groups attached to MCM-41 molecular sieves. The four-steps weight loss observed for SO₄-AlMCM-41 further verifies the interaction between the sulphate groups with the surface of MCM-41.

Fig. 4(a) shows the ²⁷Al MAS NMR spectrum of SO₄-AlMCM-41. The spectrum reveals the presence of peaks only at 0 ppm, assigned to octahedrally coordinated aluminium. It is interesting to note that the peak at 54 ppm which corresponds to tetrahedral aluminium of the framework is not observed [9,10]. The disappearance of the peak corresponding to tetrahedral aluminium indicates that after treatment with sulphuric acid, tetrahedrally coordinated aluminium was removed from the framework and transformed to octahedral aluminium, generally referred as extraframework aluminium (EFAL). However, detail examination of SO₄-AlMCM-41 spectrum reveals the presence of two peaks: a strong peak at 0 ppm and a weak peak at ~5 ppm, suggesting the existence of octahedrally coordinated aluminium with two different chemical environments. These peaks might originate from EFAL present in the form of either Al³⁺, AlO³⁻, Al₄(OH)₁²⁻ or Al₄(OSO₃H)₅⁺. The ²⁷Al MAS NMR spectrum for SO₄-AlMCM-41 after treatment with 1.0 M methanolic HCl solution, as shown in Fig. 4(d) does not exhibit any peak at the range of 0 ppm, confirming that the origin of both aluminium are extraframework.

In order to assign the two peaks observed in the sulphated AlMCM-41, quantitative ²⁷Al MAS NMR whereby a sample containing a mixture of both sulphated AlMCM-41 and aluminium sulphate (50:50) was used. Knowing that aluminium in aluminium sulphate is octahedral, we therefore matched one of the peaks to octahedral aluminium found in aluminium sulphate [19]. The spectrum in Fig. 4(a) shows that there exist two types of Al in the sulphated AlMCM-41 sample: the peak at 0 ppm is due to nonframework octahedral aluminium in aluminium sulphate, while the peak at ~5 ppm is due to octahedral aluminium bonded to EFAL (SiO–Al (OSO₃H)₅⁺). SiO⁻ attached to SiO–Al (OSO₃H)₅⁺ is less electronegative than SO₄²⁻ attached to aluminium sulphate and causes more shielding on the Al. Consequently, the signal which corresponds to EFAL would be shifted to a more negative chemical shift value. This further supports the data by TG analysis, where two distinct weight losses observed, at 200–300 and 300–600 °C, were presumably due to the decomposition of SiO–Al (OSO₃H)₅⁺ and aluminium sulphate, respectively.

Conventionally, Lewis acidity is attributed to octahedrally coordinated aluminium. Since the peak for tetrahedral aluminium was not observed by ²⁷Al MAS NMR, therefore Brønsted acidity was not expected to exist in SO₄-AlMCM-41. However, this implication contradicts that made by the pyridine-FTIR spectroscopy. Fig. 5(a) and (b) shows the pyridine-FTIR spectra of SO₄-AlMCM-41 and H-AlMCM-41, respectively. It is observed that H-AlMCM-41 exhibits bands at 1546 cm⁻¹ assigned to pyridine bound to Brønsted acid sites and at 1455 cm⁻¹ assigned to pyridine bound to Lewis acid sites [10]. This agrees with the results by ²⁷Al MAS NMR (Fig. 4(b)) where tetrahedral framework Al attributed to Brønsted acid sites and octahedral extraframework Al attributed to Lewis acid sites were observed.

²⁷Al MAS NMR studies of SO₄-AlMCM-41 sample in Fig. 4(a) did not show the presence of tetrahedral framework Al. In contrast, Fig 5(a) of SO₄-AlMCM-41 sample, showed no Lewis acid sites but possess high amount of Brønsted acid sites instead. Therefore, the existence of Brønsted acid sites in this sample, which has never been observed in similar system before, must be due to the introduction of sulphate group (HOSO₃⁻) into the sample that may have formed bond with the octahedral aluminium. The peak ratio intensity of aluminium

![Fig. 4. ²⁷Al MAS NMR spectra of (a) SO₄-AlMCM-41; (b) H-AlMCM-41; (c) cat-AlMCM-41; and (d) SO₄-AlMCM-41 after treatment with 1.0 M methanolic HCl solution.](image)

![Fig. 5. The pyridine-FTIR spectra of (a) SO₄-AlMCM-41 and (b) H-AlMCM-41 at 250 °C.](image)
sulphate to EFAL, calculated from the $^{27}$Al MAS NMR spectrum of SO$_4$-AlMCM-41, is 9:1. Since there was a large increase in the amount of Brønsted acid sites formed upon sulphation (Fig. 5(a)), therefore, it can be concluded that both nonframework aluminium sulphate and EFAL provide the sites for the formation of Brønsted acid. Besides, the intensity of the IR signal at 3740 cm$^{-1}$ attributed to silanol group decreased significantly after treatment with sulphuric acid (Fig. 6). This further indicates that the sulphate groups not only reacted with Al–OH but also with Si–OH groups, which consequently enhanced the amount of Brønsted acid sites.

The results of our studies show that the types of acid sites formed are influenced by the use of different solvents during sulphation of AlMCM-41. In all studies reported earlier, sulphation was performed in aqueous environment [12–16]. In contrast, our system was conducted in hydrophobic environment. Water which is a hydrophilic solvent would hydrolyze the sulphate groups attached to the AlMCM-41, producing Lewis acid sites. However, hydrophobic organic solvent such as dehydrated toluene which was used in this work, successfully protected the sulphate groups from being hydrolyzed and hence produced Brønsted acid sites.

The activity of SO$_4$-AlMCM-41 catalyst was tested in the Friedel-Crafts dibenzoylation reaction. In the absence of catalyst, the rate of benzoylation was very slow and dibenzoylation totally did not occur. Catalytic test results shown in Table 2 indicate that in the presence of H-AlMCM-41 catalyst, the biphenyl conversion was 83.7%. Unfortunately, the H-AlMCM-41 catalyst was inactive towards dibenzoylation of biphenyl and was unable to produce disubstituted product within 24 h. The results suggest that either the acidity of the catalyst was not strong enough or the amount of acid sites was not large enough to convert biphenyl to 4,4'-DBBP. Concentrated sulphuric acid shows 75.0% conversion of biphenyl but with poorer selectivity (35.3%) towards benzoylation. Benzoylation of biphenyl using two catalysts, H-AlMCM-41 and concentrated sulphuric acid simultaneously, gave 90.6% conversion of biphenyl but low selectivity (13.0% of 4-PBP and 1.65% of 4,4'-DBBP). On the other hand, sulphuric acid incorporated in fully amorphous silica with surface area of 43.06 cm$^2$ g$^{-1}$ was only able to give 22.3% conversion of biphenyl and produced 22.1% of 4-PBP.

<table>
<thead>
<tr>
<th>Catalyst(s)</th>
<th>Conversion of BP (%)</th>
<th>Selectivity towards 4-PBP (%)</th>
<th>Selectivity towards 4,4'-DBBP (%)</th>
<th>Selectivity towards others (%)</th>
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<tr>
<td>H$_2$SO$_4$</td>
<td>75.0</td>
<td>35.3</td>
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<td>H-AlMCM-41</td>
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<td>76.0</td>
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<td>83.2</td>
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<tr>
<td>SO$_4$-silica</td>
<td>22.3</td>
<td>22.1</td>
<td>0.0</td>
<td>0.2</td>
</tr>
</tbody>
</table>

* Homogeneous catalyst, (4-PBP), 4-benzoylbiphenyl and (4,4'-DBBP), 4,4'-dibenzoylbiphenyl.

Fig. 6. FTIR spectra of silanol groups of MCM-41 materials at 250 °C: (a) H-AlMCM-41 and (b) SO$_4$-AlMCM-41.

Fig. 7. The effect of electron density on the attack of the benzoylium ion on biphenyl (BP) and 4-phenyl benzophenone (4-PBP).
Evidently, SO$_4$-AlMCM-41 exhibited remarkable activity and selectivity. The catalyst was able to convert 94.2% of biphenyl into 83.2% of 4-PBP within 24 h, proving high performance towards benzoylation and 11.0% selectivity towards 4,4'-DBBP with no side products. The highest selectivity achieved by SO$_4$-AlMCM-41 was attributed to the uniform mesopores of 3 nm in diameter present in the MCM-41 molecular sieves, which enabled it to reduce the accumulation of the bulkier ortho- and meta-substituted products. Such phenomenon is called shape-selective effect.

The results in Table 2 also show that 4,4'-DBBP was produced when the conversion of BP exceeded 90%. This phenomenon is not only related to the amount of BP and 4-PBP in the system but also the electron density factor. The electron density in 4-PBP is lower than BP due to dislocation of electrons, which deactivates the attack of benzoylium ion by 4-PBP in order to form disubstituted 4,4'-DBBP. On the other hand, BP with higher electron density tends to attack benzoylium ion to form 4-PBP. The attack on benzoylium ion by 4-PBP becomes dominant when the concentration of BP is very low. Fig. 7 demonstrates how BP and 4-PBP attack benzoylium ion.

4. Conclusions

Sulphated AlMCM-41 (SO$_4$-AlMCM-41) mesoporous molecular sieves with SiO$_2$/Al$_2$O$_3$ ratio = 15 was prepared via impregnation of sulphuric acid using an organic solvent on the surface of H-AlMCM-41. Results of this work demonstrate that SO$_4$-AlMCM-41 is a solid Brønsted acid and active towards benzoylation and dibenzoylation of biphenyl. The production of 4,4'-DBBP is affected by the amount of acid site, amount of biphenyl and 4-PBP. The SO$_4$-AlMCM-41 was found to be active towards dibenzoylation of biphenyl reaction, giving 11.0% of 4,4'-DBBP, whereas sulphuric acid and H-AlMCM-41 catalyst only produced 4.1% of 4,4'-DBBP.

Acknowledgements

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References

Iron-porphyrin encapsulated in poly(methacrylic acid) and mesoporous Al-MCM-41 as catalysts in the oxidation of benzene to phenol

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Abstract

Poly(methacrylic acid) (PMAA) and mesoporous molecular sieve Al-MCM-41 with Si/Al = 20 were used as supports for the encapsulation of bulky iron(III)-5,10,15,20-tetra-(4-pyridyl)porphyrin (Fe-TPyP). Metalloporphyrin of Fe(III) was encapsulated inside the mesopores of Al-MCM-41 by a process of sequential synthesis of Fe-TPyP by treatment of FeCl3 with 5,10,15,20-tetra-(4-pyridyl) porphyrin (TPyP), followed by encapsulation of Fe-TPyP. Fe-TPyP complexes were also successfully encapsulated in PMAA by polymerizing a monomer (MAA) with a cross-linker around the Fe-TPyP complexes. The materials obtained were identified using XRD, UV–vis DR, FTIR and luminescence spectroscopies. The oxidation of benzene to phenol using aqueous hydrogen peroxide has been studied using both iron-porphyrin encapsulated in poly(methacrylic acid) and mesoporous Al-MCM-41 as catalysts. The encapsulated iron-porphyrin in PMAA (Fe-TPyP–PMAA) give a higher catalytic activity compared to Fe-TPyP encapsulated in Al-MCM-41 (Fe-TPyP–MCM-41). However, the product selectivity and the regenerability of Fe-TPyP–PMAA are not as good as than those of Fe-TPyP–MCM-41. One considers that the hydrophobic nature of Fe-TPyP–PMAA may account for the high catalytic activity, and the ordered structure of Fe-TPyP–MCM-41 may contribute to a high selectivity.

Keywords: Encapsulation; Iron-porphyrin; Al-MCM-41; Poly(methacrylic acid); Phenol

1. Introduction

Iron-porphyrin has been the subject of intensive study [1,2] largely because of their ability to catalyze a wide variety of oxidation transformations, e.g. alkenes epoxidation, alkenes hydroxylation, etc. with molecular oxygen. In the last two decades, therefore, increasing attention in catalytic oxidation has been focused on the use of biomimetic systems based on Fe(II), Ru(II) and Mn(II) porphyrin [3–5]. Fig. 1 shows a unique iron-porphyrin structure.

Synthetic metalloporphyrins are widely used as homogeneous catalysts for hydrocarbon oxidation [6–8]. There are, however, several disadvantages in using metalloporphyrins as catalysts in homogeneous oxidation processes. The difficulty in separating the catalysts from the product substantially increases the cost of using homogeneous catalysis in commercial processes. One approach to achieve this goal is to immobilize homogeneous catalysts on porous solid supports, which simultaneously has the advantages of turning the liquid phase oxidation from homogeneous into heterogeneous. Supporting metalloporphyrins on porous solid supports also provides a physical separation of active sites, thus minimizing catalyst self-destruction and dimerization of unhindered metalloporphyrins [9].

Mesoporous MCM-41 with its hexagonally ordered structure has attracted much attention because of their potential use as catalyst supports [10–14]. Transition metal complexes and organometallic compounds can be encapsulated in the mesoporous MCM-41 supports by physical adsorption or covalent linkage. More recently, much effort was focused on the encapsulation of metalloporphyrins in the pore of MCM-41 [15–18]. For example, Che and coworkers [18] have immobilized a ruthenium porphyrin on modified MCM-41. However, the MCM-41, an inorganic material, is hydrophilic and rigid. In this study, we also propose a procedure to encapsulate iron-porphyrin on the polymer support, namely poly(methacrylic acid) (PMAA). One expects that
the flexibility and hydrophobicity of the polymer as support give the advantages in oxidation of organic compounds. Here, we demonstrated the single step liquid phase oxidation of benzene to phenol with aqueous hydrogen peroxide over iron-porphyrin encapsulated in poly(methacrylic acid) in comparison to iron-porphyrin encapsulated in mesoporous Al-MCM-41.

Phenol is produced globally on a scale of £17 billion/year and is expected to maintain an annual growth rate of 4% through the year 2002 due to demand for bisphenol A (poly carbonate resins), phenolic resins and caprolactam (nylon 6) [19]. Phenol is currently produced industrially via the three-step cumene process. Unfortunately, this process is energy intensive, generates considerable waste, and leads to a 1:1 mixture of phenol and acetone [19]. An attractive alternative is the direct oxidation of benzene to phenol using aqueous hydrogen peroxide and a suitable catalyst. A one step process such as this would require less energy and generate zero waste, while producing only phenol.

Selective oxidation of hydrocarbons under mild conditions is of academic interest and industrial importance. In recent years, as a result of increasing environmental constraints, “clean” oxidants such as dioxygen (or air), hydrogen peroxide and alkyl hydroperoxides, which are inexpensive, is becoming more important both in industry and academia, and chemical processes based on cleaner technologies are expected to increase significantly in the next few years.

To the best of our knowledge, there is no report in open literature of the use of iron-porphyrin encapsulated in PMMA in the catalytic oxidation of benzene to phenol with aqueous hydrogen peroxide.

2. Experimental

2.1. Materials and characterizations

Unless otherwise stated, all reagents were of commercial reagent grade and used without further purification. 5,10,15,20-Tetra (4-pyridyl) porphyrin (TPyP) was purchased from Fluka (97%), FeCl3 anhydrous was purchased from Merck. Methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), α,α’-azoisobutyronitrile (AIBN) were purchased from Fluka.

The samples were characterized by X-ray diffraction (XRD) analysis using Bruker D8 Advance diffractometer with a scanning range of 29° of 1.5•10–6° using Cu Kα radiation (λ = 1.5418 Å, kV = 40, mA = 40) as the source of radiation.

Infrared spectra were recorded on Shimadzu Fourier transformed infrared (FTIR) 8300 spectrometer. The technique of KBr wafer was used by mixing about 0.25 mg sample with 300 mg KBr powder and then pressed under vacuum ca. 10 tonnes. The pellet was then put in a sample holder to determine its characteristic peaks. IR spectra were set and detected in transmittance (%) rather than absorbance unit. Twenty scans over the range 4000–400 cm–1 were carried out for all of the sample.

Ultraviolet visible diffuse reflectance (UV–vis DR) spectra were recorded on Lamda 900 spectrometer. Luminescence spectra were recorded on Perkin-Elmer LS 55 spectrometer. About 0.04 g of the sample was placed on a sample holder. After locating and locking sample holder in a proper place in the analyzer, samples were measured in the emission λ (wavelength) scale of 200–900 nm at excitation λ = 333 nm.

2.2. Synthesis of Al-MCM-41

The Al-MCM-41 with Si/Al = 20 was synthesized according to Ref. [20]. First, a clear solution of sodium silicate was prepared by combining 2.595 g of 1.00 M aqueous NaOH solution (pellet from Merck) with 10.015 g rice husk ash (90 wt% SiO2) and the resulting solution (mixture A) was then heated under stirring for 2 h at 80°C. A mixture of 1.05 g of 25 wt% aqueous NH3 solution (Merck), 9.1115 g of cetyl N,N,N-trimethyl ammonium bromide (CTABr) (Fluka) and 1.417 g of NaAlO2 (54 wt% Al2O3, Riedel-de Haen®) were put in a polypropylene bottle and the mixture (mixture B) was then heated with stirring for 1 h at 80°C. Subsequently, mixture B was added dropwise to a polypropylene bottle containing mixture A with vigorous stirring at room temperature. After stirring for 1 h at 90°C, the gel mixture in the bottle was heated to 97°C for 24 h. The CTA-aluminoisilicate gel was then cooled to room temperature. The pH of the reaction mixture was then adjusted to 10.2 by adding 25 wt% acetic acid (CH3COOH) (Merck). Repeated pH adjustments were performed in order to increase thermal stability and textural uniformity of the product. The heating and pH adjustment procedures were repeated two times. The precipitated product, as-synthesized Al-MCM-41 containing CTA-template was filtered, washed thoroughly with doubly-distilled water and dried in an oven at 97°C. Al-MCM-41 was calcined in air under static conditions in a muffled furnace. The calcination temperature was increased...
from room temperature to 550 °C for 10 h and maintained at 550 °C for 6 h.

2.3. Synthesis of iron-porphyrin (Fe-TPyP)

Iron insertion into TPyP by heating (at 100 °C) TPyP (250 mg, 0.404 mmol) and FeCl₃ anhydrous (100 mg, 0.606 mmol) at reflux in ethanol (30 ml) using oil bath for 1 h. The hot solution was filtered, washed with water and dried under vacuum.

2.4. Synthesis of Fe-TPyP encapsulated in Al-MCM-41 (Fe-TPyP–Al-MCM-41)

Fe-TPyP–Al-MCM-41 was synthesized via the method of Li et al. [9]. A suspension of Al-MCM-41 (250 mg) in methanol containing Fe-TPyP (0.24 mmol) was stirred for 24 h at 20 °C. The resulting materials was filtered and washed with CH₂Cl₂ and acetonitrile until the filtrate becomes colorless. The solid obtained was dried at 100 °C for 4 h which afforded Fe-TPyP.

2.5. Synthesis of iron-porphyrin encapsulated in poly(methacrylic acid) (Fe-TPyP–PMAA)

Fe-TPyP (1 mmol), toluene (12 ml) and MAA (4 mmol) were placed into a 25 ml glass tube and the mixture was left in contact for 10 min. Subsequently, EGDMA (20 mmol) and AIBN (30 mg) were added. The glass tube was sealed and thermostated at 60 °C in an oil bath to start the polymerization process. After 24 h, the obtained micro-spheres were air dried and weighted.

2.6. Catalytic test

Oxidation of benzene was carried out using the above catalysts. Benzene (2 ml), 30% aqueous H₂O₂ (1 ml), catalyst (50 mg) and methanol (2 ml) were placed in a glass tube and the reaction was performed with stirring at 70 °C in an oil bath. GC (Hewlett-Packard 5890 GC Series II) was used to identify the reaction product equipped with a flame ionization detector (FID) and a non-polar capillary column (carbowax). 100 µl of yields was added with 100 µl of internal standard (2-propanol in methanol). Operating conditions of GC were as follows: oven temperature, 50 °C; initial temperature, 50 °C; initial time, 5 min; rate, 10 °C min⁻¹; final temperature, 200 °C; hold time, 5 min. GC/MS (Agilent 6890N-5973 Network Mass Selective Detector) equipped with HP-5MS column (30 m × 0.251 mm × 0.25 µm) was used in order to provide some definite information about the compounds. Sample was analyzed on splitless method with helium (He) as the carrier gas. The samples (0.2 µl) were injected to GC/MS using 10 µl syringes at initial temperature 60 °C without hold time, with rate 15 °C min⁻¹ until 250 °C and hold 2 min.

3. Results and discussion

3.1. Characterization of catalysts

The FTIR spectra of Fe-TPyP, Al-MCM-41, Fe-TPyP–Al-MCM-41, poly(methacrylic acid) and Fe-TPyP–PMAA are shown in Fig. 2. The FTIR spectra of Fe-TPyP–Al-MCM-41 and Fe-TPyP–PMAA are in excellent agreement with that of neat Fe-TPyP with additional peaks due to Al-MCM-41 and PMAA, respectively (Fig. 2). The spectrum of Fe-TPyP–PMAA exhibits absorptions at 1724 cm⁻¹ (C=O) and 1159 cm⁻¹ (C–H) which are typical of PMAA, whereas absorptions at around 1100 cm⁻¹ of Fe-TPyP–Al-MCM-41 is typical of Al-MCM-41. Similarly, absorptions at 1650 cm⁻¹ (C=πN) and 1452 cm⁻¹ (C–C) are identical with that of free Fe-TPyP. The presence of Fe-TPyP is obvious, because its bands in the region 1700–1300 cm⁻¹ are not observed in the spectrum of the pure Al-MCM-41 and PMAA. This suggests that Fe-TPyPs are structurally unchanged and uniformly distributed in the PMAA and
Al-MCM-41 matrixes, which proves that Fe-TPyPs preserve their identity after immobilization. Uniform dark-purple powders were obtained in all cases indicating that iron(III) has been included in porphyrin. The IR bands of metal-complexes are weaker due to their low concentration in the PMAA and Al-MCM-41.

Fig. 3 shows the luminescence emission spectrum of Fe-TPyP–PMAA with different amount of Fe-TPyP loading. The quenching behavior of the luminescence was monitored in order to investigate what happened to the luminescence of PMAA after Fe-TPyP loading. It is clear that luminescence intensity of Fe-TPyP–PMAA at around 550 nm decreased with increase of the amount of Fe-TPyP loading. Based on the above results, it is suggested that the Fe-TPyP molecules are encapsulated in high-affinity binding to PMAA.

The Fe-TPyP encapsulated in molecular sieve Al-MCM-41 and PMAA have also been characterized by UV–vis DR spectroscopy and the typical UV–vis DR spectra are given in Fig. 4. In the UV–vis absorption spectrum, the highly conjugated porphyrin macrocycle shows intense absorption at around 400 nm (the Soret band), followed by several weaker absorptions (Q bands) at higher wavelengths (350–600 nm) [21]. Fe-TPyP presents a broad single band at 418 nm and three typical bands attributed to high spin Fe(III)-porphyrin species in the region of 500–700 nm (bands at 516, 557 and 648 nm). The presence of the band at 589 nm in the spectra of Fe-TPyP–Al-MCM-41 (Fig. 4(a)) suggests the occurrence of axial electrostatic interactions between the iron-porphyrin and the anionic Al-MCM-41 pore surfaces [22]. However, these spectra are typical for solutions, and not for the solid-state. Taking into consideration that the interaction between porphyrin is the dominant interaction in solid-state form, the encapsulation of porphyrin by MCM-41 and PMAA may cause lowering the interaction because porphyrin is now surrounded by MCM-41 and PMMA. This might be the reason why the spectra of Fe-TPyP–Al-MCM-41 and Fe-TPyP–PMAA are almost similar to that of the spectrum of Fe-TPyP in solution.

Since the external surface area of MCM-41 amounts to approximately only 10 m² g⁻¹ [23], which is related to less than 1% of total surface area, well-dispersed Fe-TPyP can only to a very small extent be situated at the external surface and therefore has to be incorporated inside the mesopores. Theoretically, the surface area of MCM-41 is sufficiently large to accommodate a well-dispersed layer of Fe-TPyP, even at loadings as high as 20 wt% Fe-TPyP in which the expected decrease of surface area of MCM-41 upon Fe-TPyP incorporation is ca. 99%. In view of the fact that calculated amount of Fe-TPyP is only ca. 1%, one should expect that only a small decrease in surface area of MCM-41 could be observed. As tabulated in Table 1 (entries 3 and 5), there was a decrease of ca. 50% in surface area of Al-MCM-41 after incorporation of Fe-TPyP. This decrease could be due to a partial blocking of pores of MCM-41 by Fe-TPyP.

The existence of Fe-TPyP in Fe-TPyP–Al-MCM-41 and Fe-TPyP–PMAA were also supported by chemical and thermal analysis (see entries 4 and 5 in Table 1). It shows that the molar amount of Fe and porphyrin is almost equal, suggesting that the catalysts contain no free Fe or TPyP.

3.2. Long-range order structure of iron-porphyrin encapsulated in Al-MCM-41

X-ray powder diffraction patterns of mesophase Al-MCM-41, calcined Al-MCM-41 and Fe-TPyP–Al-MCM-41 (Fig. 5), which are in excellent agreement with the XRD pattern for unloaded molecular sieve without any peaks arisen...
Table 1
Catalytic oxidation of benzene to phenol\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Fe ((\mu)mol)</th>
<th>Porphyrin ((\mu)mol)</th>
<th>Surface area of catalyst (m(^2) g(^{-1}))</th>
<th>Phenol yield ((\mu)mol)</th>
<th>TON per Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.0</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>Fe-TPyP</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.0</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>Al-MCM-41</td>
<td>–</td>
<td>–</td>
<td>1064</td>
<td>2.0</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>Fe-TPyP–PMAA</td>
<td>0.030(^b)</td>
<td>n.a.(^c)</td>
<td>48</td>
<td>30.0</td>
<td>1000</td>
</tr>
<tr>
<td>5</td>
<td>Fe-TPyP–Al-MCM-41</td>
<td>0.150(^b)</td>
<td>0.14(^d)</td>
<td>497</td>
<td>10.0</td>
<td>67</td>
</tr>
<tr>
<td>6</td>
<td>Fe-TPyP–Al-MCM-41 reused(^e)</td>
<td>0.150(^b)</td>
<td>–</td>
<td>–</td>
<td>10.0</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>Fe-TPyP–PMAA reused(^f)</td>
<td>0.025(^b)</td>
<td>–</td>
<td>–</td>
<td>25.0</td>
<td>–</td>
</tr>
</tbody>
</table>

\(^a\) All reactions were carried out at 70 °C for 20 h with benzene (2 ml), 30% H\(_2\)O\(_2\) (1 ml) and catalyst (50 mg) with vigorous stirring.

\(^b\) The concentration of Fe was measured absorption spectrometer.

\(^c\) Not available. We failed to determine the amount of TPyP in its mixture with PMAA.

\(^d\) The concentration of porphyrin was analyzed by Thermal Gravimetry Analyzer.

\(^e\) The reaction was performed after washing and drying of the catalyst.

3.3. Catalytic properties for oxidation of benzene

Table 1 shows the activities of iron-porphyrins for direct oxidation of benzene to phenol using aqueous H\(_2\)O\(_2\) in solution and supported on molecular sieve and polymer. Unexpectedly, reaction system containing Fe-TPyP catalyst is not active in the oxidation reaction. Fe-TPyP–Al-MCM-41 and Fe-TPyP–PMAA give higher activity than Fe-TPyP (entries 4 and 5 in Table 1). This is supported by the rate of the formation of phenol over Fe-TPyP–Al-MCM-41 and Fe-TPyP–PMAA (see Fig. 6). The most likely reason for the high activity of Fe-TPyP encapsulated in Al-MCM-41 and PMAA is the presence of Fe-TPyP coordination to molecular sieve or polymer, which render them more resistant to oxidative self-destruction.

The turnover number (TON), the molar ratio of the phenol to the loaded Fe for the reaction with Fe-TPyP–PMAA was almost 15 times higher than that of Fe-TPyP–Al-MCM-41. These observations provide strong support for the suggestion that incorporation of Fe-TPyP complexes, presumably in internal pore, occurs in Fe-TPyP–Al-MCM-41.
Fe-TPyP complexes were successfully prepared by incorporating Fe-TPyP within mesoporous molecular sieve Al-MCM-41 (Fe-TPyP–Al-MCM-41) and poly(methacrylic acid) (Fe-TPyP–PMAA) as inorganic and organic supports, respectively. The Fe-TPyP–PMAA showed higher activity compared to Fe-TPyP–Al-MCM-41. However, the regenerability of Fe-TPyP–PMAA is not as good as that of Fe-TPyP–Al-MCM-41. One considers that the hydrophobic nature of Fe-TPyP–PMAA may account for the high activity, and the ordered structure of Fe-TPyP–MCM-41 may contribute to a high selectivity.

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References

SELECTIVE DIBENZOYLATION OF BIPHENYL TO 4,4'-DIBENZOYLBPBIPHENYL OVER H-Al-MCM-41

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ABSTRACT

Dibenzyolation of benzoyl chloride in the presence of mesoporous H-Al-MCM-41 forms the biphenvyl 4,4'-dibenzozylbiphenyl (DB) with 100% selectivity. 27Al MAS NMR, pyridine adsorption and XRD data reveal that both Brnsted and Lewis acidities play a role in the production of DB and the catalytic activity is dependent on the structure of the mesoporous H-Al-MCM-41.

Keywords: H-Al-MCM-41, dibenzyolation, acidity, 4,4'-dibenzozylbiphenyl

INTRODUCTION

Benzoylation is a significant Friedel-Crafts acylation used in the commercial production of important chemicals such as benzophenone and its substituted analogues as additives in the synthesis of fine chemicals and dyes [1-5]. Recent interest is on the benzyolation of biphenvyl with benzoyl chloride, from which the monosubstituted product, 4-phenyl-benzophenone or 4-benzylobiphenyl; a useful precursor in perfumes [6], and the disubstituted product, 4,4'-dibenzozylbiphenyl (DB); an important monomer in the polymerisation of poly(4,4'-diphenylene diphénylméthane) or namely PDPV [7,8] are formed.

Current production of disubstituted 4,4'-dibenzozylbiphenyl is still via the difficult homogeneously catalysed process. Despite the increase of research activities in the field of heterogeneous catalysis, synthesis of disubstituted compound using zeolite has not so far been successful. For example, microporous zeolite beta only gives monosubstituted product as mentioned above. Although heterogeneously catalysed reactions using microporous molecular sieve did not show much potential, mesoporous molecular sieve MCM-41 is a promising alternative for reactions involving large molecules. The large internal surface area and channel apertures of the MCM-41 would allow, in principle, large molecules to access the active sites. Besides, the presence of Brnsted and Lewis acid sites in H-Al-MCM-41 play significant roles in enhancing the catalytic activity and adsorptive capacity. From this point of view, mesoporous MCM-41 molecular sieve was chosen to catalyse the dibenzyolation of biphenvyl with benzoyl chloride. This paper reports the first attempt on heterogeneous synthesis of 4,4'-dibenzozylbiphenyl over H-Al-MCM-41.

EXPERIMENTAL

Synthesis of H-Al-MCM-41

Direct synthesis of Al-MCM-41 with Si/Al ratios of 11, 45, 58, 82 were based on the following basic moly compositions: 6 SiO2 : CTABr : 1.5 Na2O : 0.15 (NH4)2O : 250 H2O. Sodium silicate solution was prepared by stirring 42.80 g of 1.00 M aqueous NaOH solution with 17.14 g colloidal silica (30 wt% SiO2) at 353 K. The sodium silicate solution was then added dropwise to a polypropylene bottle containing mixtures of 0.29 g of 25 wt% aqueous NH3 solution, 5.20 g of cetyltrimethylammonium bromide (CTABr) and NaAlO2, followed by vigorous stirring and heating at 370 K. Subsequently, the pH of the reaction mixture was adjusted to 10.2 by adding 30 wt% acetic acid (CH3COOH). The heating and pH adjustment procedures were repeated three times. The precipitated product, Al-MCM-41 with CTA template was filtered, washed, dried and calcined at 823 K overnight. H-Al-MCM-41 was prepared by ion exchange of 1 g of the calcined Al-MCM-41 sample in excess 0.5 M aqueous ammonium nitrate solution (NH4NO3) overnight at 353 K, followed by washing, air-drying and calcination of the NH4+ samples at 773 K for 4 hours. H-Al-MCM-41 samples with Si/Al ratios of 11, 45, 58 and 82 are labelled as HAM-1, HAM-2, HAM-3 and HAM-4 respectively.
Characterisations

X-ray powder diffraction (XRD) patterns were recorded on a Siemens D5000 powder diffractometer with Cu $K_{x}$ radiation. The BET surface areas and the pore size distributions were measured on a Micromeritics volumetric adsorption analyzer (ASAP 2010). Ammonia-TPD spectra were measured using Thermoquest TPDRO 1100, in which the desorbed NH$_{3}$ was recorded using a thermal conductivity detector. The samples were purged at 393 K in a nitrogen stream for 1 h. NH$_{3}$ was adsorbed at 393 K. Desorption of NH$_{3}$ was initiated by heating the sample continuously in a 0.5 mLs$^{-1}$ flow of nitrogen up to 873 K at a heating rate of 10 Kmin$^{-1}$ in a helium flow as the carrier gas. Infrared spectra of pyridine adsorbed on mesoporous H-Al-MCM-41 were recorded on Shimadzu FTIR 8300 spectrometer using self-supporting wafer. Pyridine was adsorbed onto the sample for 5 minutes and desorbed at 298 K and 423 K under 10$^{-2}$ mbar for 1 hour. $^{29}$Si MAS NMR spectra were recorded on a Bruker 400 MHz Avance at a frequency of 79.5 MHz, spinning at 10 kHz using 45$^\circ$ pulses with a relaxation delay of 600 seconds. $^{27}$Al MAS NMR spectra were recorded at a frequency of 104.2 MHz, spinning at 7 kHz using 1.9 usec pulses with 2 seconds relaxation time delays and 6000 scans.

Catalysis

H-Al-MCM-41 sample was activated in a sintered glass tube under a nitrogen gas flow and heated at 523 K for 4 hours. The liquid phase acylation of biphenyl with benzoyl chloride was carried out in a 50 mL two necked flask attached to a condenser and supplied with nitrogen gas. The temperature of the reaction vessel was maintained at 353 K using an oil bath. Biphenyl (0.001 mol), benzoyl chloride (0.01 mol), nitrobenzene (6 mL) and H-Al-MCM-41 (0.5 g) were slowly added, followed by stirring and heating for 3 hours. The resulting products were analysed by gas chromatography (GC-HP 6890/ Ultra-1 column/FID) and verified by gas chromatograph-mass selective detector (GC-MSD/Agilent Technologies). Each sample was analysed by the splitless method using helium as the carrier gas.

RESULTS AND DISCUSSION

Characterisation of H-Al-MCM-41

X-ray diffractograms of H-Al-MCM-41 samples in Figure 1 consist of up to four reflections typical of hexagonal lattice structure of mesoporous MCM-41; indexed as (100), (110), (200), (210) respectively. The strong intense (100) peak observed indicates that the long-range order of the sample is retained. A less intense (100) reflection was observed in sample HAM-1 which suggests that there is an increase in disorder of the sample, which must has resulted during the ion exchange modification. Although the NH$_{4}^{+}$ ions prefer to be ionically bonded to the negatively charged Al atoms in the framework, it is evident that sample HAM-1 with a high amount of framework Al atoms could not withstand the massive amount of NH$_{4}^{+}$ ions; causing the framework to collapse.

Table 1. Physical properties of H-Al-MCM-41 and yield of 4,4′-dibenzoylbiphenyl (DB).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al ratio*</th>
<th>Surface Area (m$^{2}$/g)</th>
<th>Total amount of adsorbed ammonia (mmol/g)</th>
<th>Yield of DB (μmol) **</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAM-1</td>
<td>11</td>
<td>1093</td>
<td>1.19</td>
<td>0.21</td>
</tr>
<tr>
<td>HAM-2</td>
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<td>943</td>
<td>1.21</td>
<td>0.32</td>
</tr>
<tr>
<td>HAM-3</td>
<td>58</td>
<td>1171</td>
<td>0.96</td>
<td>0.36</td>
</tr>
<tr>
<td>HAM-4</td>
<td>82</td>
<td>1186</td>
<td>1.48</td>
<td>0.45</td>
</tr>
</tbody>
</table>

* Si/Al ratios are calculated from the SiO$_{2}$:Al$_{2}$O$_{3}$ mole ratios of as-synthesised Al-MCM-41 starting materials in the formation of the gel composite.

** Reactions were carried out in 3 hours.

Surface areas calculated from nitrogen adsorption analysis and tabulated in Table 1 confirm the mesoporosity of MCM-41. Data from TPD profiles of NH$_{3}$ adsorption in Table 1 indicate the presence of physisorbed ammonia in all samples.
In order to determine the acid strength of Lewis and Brønsted acid sites, pyridine adsorption analysis as monitored in situ with infrared spectroscopy was carried out for all samples. Figure 2 shows the pyridine desorption FTIR spectra of samples HAM-3 and HAM-4 at 298 K and 423 K. FTIR spectra of samples HAM-1 and HAM-2 show similar characteristics and are not shown here. As observed, Lewis and Brønsted acid sites appear at 1450 cm\(^{-1}\) and 1550 cm\(^{-1}\), respectively. Generally, in all samples, pyridine was more adsorbed on the Lewis acid sites rather than the Brønsted acid sites. In fact, sample HAM-3 shows a balance in the strength of Lewis and Brønsted acid sites and, compared to other samples, the strengths are indeed weaker at the beginning of pyridine desorption. The presence of Lewis acid sites in most samples suggests that extraframework Al (EFAL) are likely to exist on the structure of H-Al-MCM-41; which was confirmed by \(^{27}\)Al MAS NMR analysis.

The \(^{27}\)Al MAS NMR spectra of H-Al-MCM-41 with various Si/Al ratios in Figure 3 show a broad peak at ca. 53 ppm; confirming the incorporation of aluminium into the framework of MCM-41 as tetrahedral aluminium (Al\(_{tet}\)) whereas the intense peak at 0 ppm indicates that octahedral aluminiums (Al\(_{oct}\)) are present as EFAL. EFAL may be present in many forms, such as Al\(^{3+}\), AlO\(^{+}\), Al(OH)\(^{2+}\) and charged Al\(_2\)O\(_4\)\(^{3-}\) clusters within the catalyst [9]. The relative areas of the peaks as measured from their intensities indicate that
samples HAM-1 and HAM-4 contain higher amount of tetrahedral Al compared to samples HAM-2 and HAM-3. In addition, the sharp and intense peak assigned to octahedral aluminium observed in samples HAM-2, HAM-3 and HAM-4 reflects the chemical equivalence of the highly mobile EFAL on H-Al-MCM-41 structure.

The presence of EFAL on H-Al-MCM-41 was further verified by treatment with methanolic HCl solution [10]. $^{27}$Al MAS NMR of EFAL containing sample HAM-4 after treatment with methanolic HCl solution as shown in Figure 5, exhibits only a single broad peak of tetrahedral aluminium, confirming that octahedral aluminium or EFAL has been removed.

![Figure 3. $^{27}$Al MAS NMR spectra of calcined H-Al-MCM-41 samples of various Si/Al ratios.](image)

![Figure 4. $^{27}$Al MAS NMR spectra of sample HAM-4: (a) before treatment and (b) after treatment with 1.0 M of methanolic HCl solution.](image)
Catalysis

Analysis by gas chromatography indicates that 4,4'-dibenzoylbiphenyl was the only product formed; implying the presence of Lewis acid sites in all the catalytic systems used. Catalytic results in Table 1 indicate that samples with higher Si/Al ratios produced higher yields of 4,4'-dibenzoylbiphenyl. Sample HAM-4 with the highest Si/Al ratio produced 0.45 μmol 4,4'-dibenzoyl biphenyl; the highest yield, after 3 hours of reaction. Sample HAM-1 produced a low quantity of 4,4'-dibenzoylbiphenyl although it contains a high amount of Al since its structure has collapsed as explained in Section 4.1. It is noted that the steep increase in the yield of 4,4'-dibenzoylbiphenyl occurs during the first hour of reaction (Figure 5). The catalytic test results indicate that the product yield is influenced and determined by the presence of both Lewis and Brønsted acid sites. The results in Figure 5 also show that the yield of the product was reaching saturation for all samples after 1 hour of reaction time; due to deactivation as a consequence of deterioration in crystallinity of the catalyst. Indeed, sample HAM-1 being the least crystalline to XRD (Figure 1) gave the lowest yield of product.

![Figure 5. Effect of reaction time on the yield of 4,4'-dibenzoylbiphenyl over H-Al-MCM-41.](image)

![Figure 6. Proposed mechanism of the benzylation of biphenyl with benzoyl chloride over H-Al-MCM-41.](image)

Although the conversion calculated is very low (<0.05%), this is the first example of successful formation of disubstituted 4,4'-dibenzoylbiphenyl. Our study has demonstrated that Al-MCM-41 plays a role in the catalytic system and induces the production of DB, which was not achieved using homogeneous AlCl₃
system by itself. However there is a possibility that the homogeneous AlCl₃ present also contribute towards the reaction and is currently being studied. The mechanism of the formation of 4,4'-dibenzoylphenyl using EFAL is proposed in Figure 6; however the influence of framework Al or Brønsted acid sites in the mechanism is not yet understood.

CONCLUSION

The production of 4,4'-dibenzoylphenyl catalysed by mesoporous H-Al-MCM-41 is achieved with 100% selectivity. The presence of EFAL and framework Al affect the reactivity of H-Al-MCM-41 catalyst and the yield of DB.

ACKNOWLEDGEMENT

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REFERENCES

EFFECT OF LOADED ALKALI METALS ON THE STRUCTURAL, BASICITY AND CATALYTIC ACTIVITY OF ZEOLITE BETA

WONG KAH MAN¹, ZAINAB RAMLI² & HADI NUR³

Abstract: Zeolite Beta was modified by incorporation of an alkali metal (Na, K, Cs) through wet impregnation method. The incorporation of the base guesta has reduced the crystallinity and BET surface area of zeolite Beta, as evidenced by XRD, IR and nitrogen adsorption characterizations. The framework structure was totally collapsed at ≥ 8% w/w loading of Na and K. Nevertheless, the concentration of base sites (basicity) was enhanced as evidenced by the increase in the amount of desorbed CO₂ in TPD-CO₂ as the amount of metal loading increases. The catalytic activity of the modified samples was tested in dehydration-dehydrogenation of cyclohexanol. Selectivity of cyclohexanone that is produced on base sites of zeolite Beta increased with the increase in the basicity, consequently suppressed the selectivity of cyclohexene produced at acidic sites. Cyclohexene was obtained as the dominant product due to the dominant acidic properties of zeolite Beta. The ratio of cyclohexene to cyclohexanone varies with the increase in the metal loading.

Keywords: Base zeolite Beta, alkali metal, basicity, dehydration-dehydrogenation of cyclohexanol

1.0 INTRODUCTION

The knowledge of basicity enhancement in zeolite by cation exchange and incorporation of new species, such as hydroxides, oxides, and alkaline metal clusters, has been used for many years [1]. At the beginning of the 1990s, zeolites were used as base

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catalysts in their ion exchange and impregnate forms. Ion exchanged zeolites possess only low strength of base sites. In order to create stronger base sites in the cavities of zeolites, impregnation with various alkali salts was carried out. The base sites of the guest oxides were shown to be stronger than those of the zeolitic framework [2].

The main obstacle in preparing base zeolite is the low resistance of the framework structure towards basicity, wherein the structure will collapse due to the hydrolysis of Si-O-Al bond in the zeolite framework. In this work, zeolite Beta was chosen to be modified into base catalysts due to its large pore structure which is desirable for catalysts modification and catalytic activity by larger organic molecules. It also has the potential in exhibiting base property that is greater than expected from its chemical composition alone [1].

In this study, zeolite Beta with base property was prepared by introducing an alkali metal (Na, K and Cs) through wet impregnation method. The structural and basicity properties of the samples were characterized by XRD, FTIR, nitrogen adsorption and TPD-CO$_2$ in order to correlate their catalytic activity in the dehydrogenation-dehydration of cyclohexanol as model reaction.

2.0 EXPERIMENTAL

2.1 Preparation of the Catalysts

Zeolite Beta in hydrogen form (HBeta) with SiO$_2$/Al$_2$O$_3$ = 25 supplied by Zeolyst was used as the starting material. Catalysts were prepared by wet impregnation using the alkali metal acetate (Na, K and Cs) with various percentages [3]. Alkali metal acetate was dissolved in distilled water and then added to zeolite HBeta. The mixture was mixed homogenously using a magnetic stirrer. The ratio of the weight of zeolite to the volume of distilled water used to dissolve the metal salt was 1:3. The mixture was left to dry slowly in a desiccator containing silica gel, by stirring overnight, followed by oven drying at 100°C overnight. The dried samples were calcined at 500°C for 6 hrs in air with a heating rate of 1°C/min where the metal salt decomposed into its oxide form. Samples were labeled as stated in Table 1.

2.2 Characterizations

The prepared samples were characterized by XRD, IR and nitrogen adsorption. The XRD diffractogram was recorded on D500 Siemens Kristalloflex X-ray diffractometer with CuK$_\alpha$, as the radiation source with $\lambda$ = 1.5418 Å at 40 kV and 30 mA. Diffractions were measured in the range of 20 of 2° to 60° at room temperature with step time of 0.02°s. The infrared spectra was recorded at room temperature with 4 cm$^{-1}$ resolutions between 4000-400 cm$^{-1}$ by using FTIR Perkin Elmer 1600 series. The BET surface area of the modified catalysts were determined by nitrogen adsorption using automated adsorption instrument Micromeritics ASAP 2010 model as well as ThermoFinnigan Qsurf Surface Area Analyzer M1-M3.
2.3 Catalytic Reaction

Dehydration-dehydrogenation of cyclohexanol was carried out using a down-flow, fixed bed reactor of 8 mm internal diameter at atmospheric pressure [4]. The catalyst (0.1 g) was pretreated in the reactor at 300°C for 2 hrs. Oxygen was then passed through the catalytic bed and followed by feeding of the reactant at the flow rate of 6 mL hr⁻¹. The reaction was carried out at 300°C for 1 hr. The product in liquid form was collected at the bottom of the reactor and analyzed by a Hewlett Packard Model 5890A gas chromatography with Flame Ionization Detector (FID). Analysis was carried out from 40-200°C at the heating rate of 10°C min⁻¹ by using Phase AT-WAX capillary column (diameter 0.25 mm, film thickness 0.2 μm, length 30 m).

3.0 RESULTS AND DISCUSSION

3.1 Physical Properties

The XRD diffractograms for samples of Na- and K-impregnated HBeta after calcination are shown in Figures 1 and 2. The samples are noted as Na-X or K-X where X denotes the percentage of metal loading. The diffraction pattern for samples with 1 - 4%w/w of metal loadings (Na-1, Na-2 Na-4, K-1, K-2, K-4) shows similar pattern to that of the parent HBeta as indicated by the diffraction peaks at 2θ = 7.8°, 16.5°, 2.15°, 22.5°, 25.3°, 26.9°, 29.5° and 43.5°. The presence of all the typical XRD peaks for zeolite Beta [5], indicates the framework structure has been retained after loaded with these percentages of sodium and potassium. However, diffractograms for samples Na-6 and K-6 show partial amorphous phase suggesting that the framework of zeolite Beta have partially collapsed. Meanwhile, samples Na-8 and K-8 have turned into completely amorphous, indicating a total collapse of the zeolite framework.

On the other hand, framework structures of Cs-impregnated HBeta samples were retained even at 8%w/w of cesium loading (Figure 3). Since cesium has far higher atomic weight compared to sodium and potassium, in a same %w/w of alkali metal in zeolite Beta, cesium has the lowest number of mole. Consequently, the framework was not affected by the presence of cesium with the small amount of cesium loading.

There is no indication of the presence of any crystalline phase such as alkali metal (Na, K, Cs) acetate or new alkali metal phase, other than the Beta phase. It shows that
Figure 1  X-ray diffraction patterns of the sodium impregnated HBeta after calcination: (a) HBeta, (b) Na-1, (c) Na-2, (d) Na-4, (e) Na-6, (f) Na-8. The number denotes % of metal loading.

Figure 2  X-ray diffraction patterns of the potassium impregnated HBeta after calcination: (a) HBeta, (b) K-1, (c) K-2, (d) K-4, (e) K-6, (f) K-8. The number denotes % of metal loading.

Figure 3  X-ray diffraction patterns of the cesium impregnated HBeta after calcination: (a) HBeta, (b) Cs-1, (c) Cs-2, (d) Cs-4, (e) Cs-6, (f) Cs-8. The number denotes % of metal loading.
the alkali metal salt or oxides are well dispersed on the surface of zeolite Beta crystal [6]. However, the intensity of XRD peak at 2θ = 22° decreases with the increase in metal loading, indicating the decrease in the crystallinity of zeolite Beta framework structure (Table 1). The relative crystallinity of both sodium and potassium impregnated zeolite Beta decreased successively with an increase of the metal loading. The degree of crystallinity of potassium impregnated Hbeta sample was found to be lower compared with the sample of sodium impregnated Hbeta. This might be due to the higher alkalinity of potassium, as the potassium is more electropositive than sodium. Thus, it is expected that the hydrolysis of Si-O-Al will be greater in potassium-impregnated samples. Conversely, the crystallinity of cesium impregnated samples decreased monotonously due to the lesser number of mole Cs loading.

The results revealed that the presence of alkali metal oxides affected the thermal stability of zeolite Beta, leading to the deterioration and collapsed of the framework structure when calcined at elevated temperature. This may be due to the hydrolysis of Si-O-Al bond by alkali during calcination. Apart from that, the formation of alkali metal-aluminosilicate due to the strongly base condition during the impregnation procedure may also lead to partial damage of zeolite framework [7].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal loading (%w/w)</th>
<th>Relative crystallinity (%)</th>
<th>BET surface area (m²/g)</th>
<th>Amount of desorbed CO₂ (µmole/g)</th>
<th>Amount of desorbed CO₂ (mole CO₂/mole metal)</th>
</tr>
</thead>
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<td>100.00</td>
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<td>23.02</td>
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<tr>
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<td>55.94</td>
<td>492.14 Reserved</td>
<td>7.69</td>
<td>12.78</td>
</tr>
</tbody>
</table>

* Intensity of the peak at 2θ=22° in comparison with the parent Hbeta (%)
* Determined by nitrogen adsorption using BET technique (Micrometrics ASAP)
* Amount of desorbed CO₂ determined by TPD-CO₂
* ThermoFinnigan Qsrf Surface Area Analyzer
The BET surface area of zeolite Beta was found to decrease as the metal loading increased (Table 1). This could be attributed to the dissolution of part of the framework during impregnation and pore filling by the alkali oxides [8]. This is supported by the fact that the BET surface area decreases linearly as a result of the decrease in the crystallinity of zeolite Beta framework with the value of calibration curve $R^2$ of 0.9319. The drastic decreased of about 87 and 86% in the BET surface area of samples Na-8 and K-8, respectively in comparison to HBeta, indicated the collapse of the framework structure. On the other hand, the BET surface area of Cs-8 sample still remained more or less similar to that of the HBeta. This findings support the results obtained from XRD and IR analyses indicating that the framework structure of Cs-8 was still retained even at 8%w/w Cs loading.

### 3.2 Basicity Study

The TPD-CO$_2$ thermograms of sodium impregnated zeolite Beta samples are as shown in Figure 4, while the data of TPD of desorbed CO$_2$ are presented in Table 1. It was observed that most of the CO$_2$ was desorbed from the catalyst at temperature below 200°C with the maximum desorption peak at around 100°C. This indicates the presence of weak base sites in zeolite Beta where at this temperature range, the CO$_2$ is physically attached to the surface of the zeolite Beta samples. Both potassium (Figure 5) and cesium (Figure 6) impregnated zeolite Beta showed similar results as the sodium impregnated samples.

The shift of the desorption peak to a slightly higher temperature in samples Na-6, Na-8, K-6 and K-8 implies a slight increase in basicity of these samples. It suggests that the bulkier loading of sodium may have forced the occupancy of the sodium oxides into the small cages of the zeolites (i.e. double six or four rings cages) rather than in the channel systems. A slightly higher energy is needed to desorb the CO$_2$ attached like this fashion (in the small cages) and thus resulting in higher temperature for desorption for these samples. However, the strength of the basicity of sample Na-8 and K-8 is slightly lower in which the maximum desorption temperature occur at slightly lower temperature than samples Na-6 and K-6. This may be due to the fact that the framework structure of zeolite Beta at 8%w/w of sodium and potassium loading may have collapsed causing the sodium oxides dislocated on to the amorphous surface of SiO$_2$ and Al$_2$O$_3$.

Even though CO$_2$ adsorbed weakly on the catalysts, the obtained TPD data do reveal some correlation in the basicity of the catalysts. The basicity of parent HBeta increased to about 60% or more than 2-fold, respectively with the 1% and 2% w/w loading of sodium (Table 1). The basicity was found to increase with an increase of the percentage of sodium loading, in which it achieved 7-fold increment in 8%w/w of sodium loading. The base guest, i.e. sodium oxide was found to contribute to the basicity that was created after calcinations at high temperature. However, an additional desorption peak was observed in sample Na-6 which might be contributed by the
**Figure 4** TPD-CO$_2$ thermograms of the sodium impregnated HBeta: (a) HBeta, (b) Na-1, (c) Na-2, (d) Na-4, (e) Na-6, (f) Na-8. (The number denotes % of metal loading)

**Figure 5** TPD-CO$_2$ thermograms of the potassium impregnated HBeta: (a) HBeta, (b) K-1, (c) K-2, (d) K-4, (e) K-6, (f) K-8. (The number denotes % of metal loading)
decomposition of acetate residue, such as acetate, in the sample. Meanwhile, the basicity remained the same when 1%w/w and 2%w/w of potassium were loaded into zeolite Beta samples (Table 1). However, the basicity increased more than 2-fold when 4%w/w of potassium was loaded. The basicity increased exponentially when 8%w/w and 8%w/w of potassium were impregnated, reaching ~35 μmole/g and ~45 μmole/g, respectively.

Cesium oxide is known as a strong base. Thus, a higher basicity is expected when cesium oxide was introduced into zeolite Beta. However, the results showed no significant increment in the basicity. This may be due to the small amount of the number of mole cesium used to impregnate the zeolites (even at 8% loading,). Nonetheless, the base strength was enhanced slightly by the small amount of cesium introduced into HBeta. This could be seen as a slight shift of desorption peak at −260° towards higher temperature as the cesium loading is increased, as shown in Figure 6.

In general, the number of basic sites created by the introduction of sodium into zeolite Beta framework is higher than potassium and cesium (Table 1), except for 8%w/w loading, which is slightly lower than sample K-8. Potassium is found to have a higher contribution to basicity strength in comparison to sodium, where it needs about 2-fold more amount of number of mole sodium in comparison to potassium in order to achieve the basicity (> 40 μmole/g) as contributed by potassium. The number of moles of CO₂ desorbed per mole of alkali metal was found to decrease as %w/w of the
metal loading increased. This may be due to the lower dispersion of metal oxides and the tendency to form metal oxides cluster in samples containing higher amounts of metal oxides [8]. The role of cesium as a highly alkali metal precursor was insignificant in this study, due to its small amount of mole cesium loading compared to that of the sodium and potassium impregnated zeolite Beta.

3.3 Catalytic Activity

The dehydration dehydrogenation of cyclohexanol was used as the model reaction to test the catalytic activity of the alkali metal impregnated zeolite Beta. Results from the catalytic testing are summarized in Table 2.

By using alkali metal impregnated zeolite Beta as catalyst, the selectivity of cyclohexanone was found to increase as the amount of sodium and potassium loading increased, especially at a 6-8% w/w of metal loading with basicity higher than 30 μmole/g (Figure 7). The significant increase in the selectivity of cyclohexanone from 4% w/w to 6% w/w loading is due to the slightly stronger basicity besides its higher amount of basicity alone. Meanwhile, the selectivity of cyclohexanone slightly dropped at 8% w/w loading of sodium and potassium due to the collapse of zeolite Beta framework, where the base strength is slightly lowered. The fact that the slightly weaker basicity, due to the collapsed zeolite Beta framework, causing the slight decrease in selectivity of cyclohexanone suggests that the framework of zeolite Beta does have an influence in catalyzing this reaction.

Table 2 Catalytic activity of alkali metals loaded zeolite Beta catalysts on the hydration-hydrogenation of cyclohexanol

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Cyclohexene</th>
<th>Cyclohexanone</th>
<th>Cyclohexene / cyclohexanone</th>
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<td>HBeta</td>
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<td>80.74</td>
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<td></td>
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</table>
**Figure 7** Influence of alkali metal loading (%w/w) on the selectivity of cyclohexanone

**Figure 8** Influence of alkali metal loading (%w/w) on the selectivity of cyclohexene
The selectivity of cyclohexanone increased to about 7 and 5-fold for sample K-6 and K-8 compared to that of the parent HBeta (Table 2). The selectivity of cyclohexanone is even far more higher in sample Na-6 and Na-8 with 13 and 8-fold of increment respectively. The higher selectivity of cyclohexanone in sodium impregnated zeolite Beta than the potassium may be due to the larger amount of sodium that have been loaded, which is about 2-fold of millimole higher in comparison to potassium. There is no increment in the selectivity of cyclohexanone (Figure 7) when using the cesium impregnated zeolite Beta as catalyst (Cs-1 to Cs-8) due to the low basicity that has been created. Thus, cyclohexene which is produced at acid sites is largely obtained by using these catalysts with high selectivity, i.e. > 93%.

Cyclohexene is found to be the main product obtained in this reaction. This indicates that the basicity created by the introduction of an additional guest is incomparable to the inherently acidic properties in zeolite Beta. However, the higher percentage of alkali metal loading would suppress the selectivity of cyclohexene (Figure 8), except for cesium impregnated zeolite Beta. This shows some competition between acidic and basic properties in this reaction as the basicity increases (Table 2). The selectivity

![Figure 9](image_url)  
*Figure 9* Influence of alkali metal loading (%w/w) on the conversion of cyclohexanol
of cyclohexene decreased significantly as 6-8%w/w of sodium and potassium was introduced into zeolite Beta. The ratio of selectivity of cyclohexene to cyclohexanone was found to decrease as the zeolite Beta loaded with alkali metals (Na and K). Thus, the increase in the basicity will suppress the acid sites in zeolite Beta causing the decrease in the selectivity of cyclohexene. The conversion of cyclohexanol (Figure 9) is also decreased in parallel with the decrease in selectivity of cyclohexanone and relative crystallinity.

4.0 CONCLUSIONS

The basicity of zeolite Beta was enhanced by the introduction of an additional alkali metal as a base guest. The basicity increased with the increase in the amount of metal loading but simultaneously decreased in both crystallinity and the surface area. At a higher amount of metal loading and elevated temperature, the stability of zeolite framework decreased due to the hydrolysis of Si-O-Al bond in the present of alkali metals. The selectivity of cyclohexanone increased with the increase of basicity. However, cyclohexene remains the main product in this reaction, indicating the basicity that has been created is still incomparable to the inherently acidic properties in zeolite Beta. The increased in basicity will inherently suppressed the acidic property in zeolite Beta, as evidence by the decrease in the ratio of cyclohexene to cyclohexanone. Samples of zeolite Beta loaded with 6%w/w Na and K respectively were found to be the best catalyst in this study, wherein the basicity was enhanced significantly without collapsing the framework structure of zeolite Beta besides increasing the selectivity of cyclohexanone.

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The Basicity and Acidity of Beta Zeolites after Ion-Exchange with Alkali Metal Cations: a Physicochemical Characterization

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ABSTRACT: The structure, basicity and acidity properties of the alkali metals (Na, K and Cs) exchanged zeolite beta were investigated in this work. Infrared (IR) and X-ray diffraction (XRD) were used for structural characterizations, while Temperature programmed desorption (TPD) of CO₂ and NH₃ were used for the determination of basicity and acidity, respectively. Results reveal that the framework structure of zeolite beta is retained after the exchange but with a successive decrease in the relative crystallinity after the modification. The acidity of zeolite beta was strongly affected by the crystallinity of the ion-exchanged zeolite beta, in which the acidity has decreased significantly with the decrease in the crystallinity. However, the basicity after the exchange was not very significant in comparison to the acidity. The effect of the crystallinity and the type of alkali metal cations on basicity is also shown.

KEYWORDS: acidity, basicity, zeolite beta, ion-exchange, alkali metal cation

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1 INTRODUCTION

The acidity and basicity of zeolites plays an important role in their catalytic and adsorption properties. For instance, heterogeneous acid catalysis by zeolites has been intensively investigated especially in the petroleum refining and cracking process [1]. In addition, the basicity is important in processes that require catalytic acid-base pairs, e.g. alcohol dehydrogenation or selective sorption and separation [2]. Thus, fundamental studies on heterogeneous basic catalysts become necessary in order to achieve the success like those heterogeneous acid catalysts.

Zeolite is reported having base property. The fascinating of basicity in zeolitic materials was reviewed recently by Hattori [2] and Barthomeuf [3-5]. According to Barthomeuf, acids and bases are conjugated, where the existence of protons in zeolites has to be associated with that of basic sites. The origin of basicity in zeolite is due to the oxygen atom derived from alumina tetrahedral. Basicity of zeolite can be enhanced by changing the electronegative charge of the framework and or by introduction of basic guest in their structure [2-7].

Studies on base zeolite have usually focused on the faujasites structure due to their high aluminum content. Quite a number of reports reviewed the effectiveness of the base zeolite X and Y in the base catalyzed reaction [8-10]. However, some other zeolitic materials, which have not yet been investigated with regards to their basicity, might have interesting base structure and character.

Zeolite beta is a high-silica and large pore crystalline aluminosilicate material. The framework structure of zeolite beta possesses three-dimensional 12-membered ring pores with an interconnected channel system [11]. Zeolite beta has high thermal stability and large pore property that desirable for catalyst modification and catalytic activity. It was reported that zeolite beta possess base properties that are greater than expected from its low aluminum chemical composition alone [3, 12]. Nevertheless, only several attempt have been reported in preparing base zeolite beta [12-14]. Here, we study the acidity and basicity of zeolite beta after ion-exchange with alkali metal cations by using Temperature programmed desorption (TPD) of CO₂ and NH₃, X-ray diffraction (XRD) and Fourier transform infrared (FTIR) in order to corre-
late the acidity and basicity with the structural properties.

2 EXPERIMENTAL

2.1 Preparation

Protonic zeolite beta (HBeta) with SiO2/Al2O3 = 25 supplied by Zeolyst was used as a starting material in this study. Alkali metal (Na, K, Cs) exchanged zeolite beta were prepared by adding HBeta into 1.0 M aqueous solution of the corresponding metal nitrate or acetate at 80 ~ 90°C and stirred overnight. The ratio of zeolite to volume of metal solution that used was 1 : 10 g/ml. It was then filtered and washed with distilled water. This procedure was repeated for six times. Finally, it was dried at 100°C overnight and calcined in air at 500°C for 6 hours with the heating rate of 1°C/min. The exchanged zeolite was labeled as MBeta, where M referred to the alkali metals (Na, K and Cs).

2.2 Characterizations

The exchanged zeolites samples were characterized by XRD and IR. The diffractogram was recorded on D500 Siemens Kristaloflex X-ray diffractometer with CuKα as the radiation source with λ = 1.5418 Amstrong at 40 kV and 30 mA. Samples were measured in the range of 2θ of 2° to 60° at room temperature with step time of 0.02°/s. The FTIR spectra were recorded at room temperature with 4 cm⁻¹ resolutions between 4000 ~ 400 cm⁻¹ by using FTIR Perkin Elmer 1600 series. While, the IR spectra of hydroxyl groups for the exchanged zeolite beta were recorded on the FTIR Shimadzu 8000 series. Self-supported wafers (~ 10 mg) were heated at 400°C under vacuum for 2 h. The spectra were then recorded at room temperature in absorbance mode with 2 cm⁻¹ resolutions.

The basicity property of the prepared base zeolite beta was characterized by TPD-CO2, acquired using TPD/R/O 1100 ThermoFinnigan. Sample weighing 0.15 ~ 0.25 g was pretreated in a flow of nitrogen at 400°C for 2 h. Sample was then exposed to CO2 at a rate of 20 ml/min for 30 min at 40°C. The temperature was raised from 40 ~ 600°C. The desorbed gases were analyzed by TCD. TPD-NH3 has also been carried out with the same condition. The samples were pretreated at 450°C and the NH3 is adsorbed at 80°C.

3 RESULTS AND DISCUSSION

3.1 Physical properties

The XRD diffraction pattern of the exchanged zeolite beta is shown in Fig. 1. Peaks at 7.8°, 16.5°, 21.4°, 22.5°, 25.3°, 26.9°, 28.8°, 29.5° and 43.5° were observed. Both intense peaks at 7.8° and 22.5° are assigned to the d001 and d002 respectively, as reported by Peres-Periante et al. [15]. The broad peaks at 7.8° is the characteristic peak for the faulted structure, while the sharp peak at 22.5° is due to the tetragonal and monoclinic symmetry structure of zeolite beta. The presence of all the typical diffractions peaks of zeolite beta (Fig. 1) in each sample indicates the retaining of the framework structure of zeolite beta after ion exchanging with 1.0 M aqueous solution of alkali metal cations, i.e. Na⁺, K⁺ and Cs⁺. However, the intensity of the diffraction peaks of the exchanged samples decreases consecutively after the exchanged indicating the deterioration of the crystal structure of zeolite beta has occurred.

FIGURE 1: X-ray diffraction patterns of the exchanged zeolite beta: (a) HBeta, (b) NaBeta, (c) KBeta and (d) CsBeta.

FIGURE 2: IR spectra of the exchanged zeolite beta: (a) HBeta, (b) NaBeta, (c) KBeta and (d) CsBeta.
The basicity and acidity of Beta...

Figure 3: IR spectra of the exchanged samples after heated at 400°C for 2 h under vacuum: (a) HBeta, (b) NaBeta, (c) KBeta and (d) CsBeta.

The relative crystallinity of the exchanged zeolite beta was tabulated in Table 1. It was calculated based on the intensity of the peak at 22° in comparison with the parent HBeta. It is shown that the relative crystallinity of zeolite beta decreases with the increase in size and the electropositive character of alkali metal cations, in the order of Na⁺ < K⁺ < Cs⁺. It was suggested that the decrease in the crystallinity might be due to the strong interaction of the cation with the oxygen atom of the alumina tetrahedral in the zeolite framework. As the electropositive characteristic of the cations increased from Na⁺ to Cs⁺, the stronger interaction of the cations with the oxygen atoms of the alumina tetrahedra is expected, thus weaken the bond of the oxygen with the rest of zeolite framework. It then explained the decrease of about 60% of the crystallinity of CsBeta compared to the parent HBeta.

The IR spectra of the exchanged zeolite beta samples are shown in Fig. 2. There are several typical bands that can be observed in the spectrums for all samples. The bands in the region of 1250 ~ 1200 cm⁻¹, 1100 ~ 1050 cm⁻¹ and 800 ~ 750 cm⁻¹ are assigned to the external asymmetric stretching, internal asymmetric stretching and symmetric stretching of TO₄ (T = Si, Al) respectively. The double 6-membered ring and double 4-membered ring vibrations that can be observed respectively at 570 ~ 560 cm⁻¹ and 520 ~ 510 cm⁻¹ indicate the framework structure of zeolite. Meanwhile, band at around 462 cm⁻¹ is assigned to the T – O bending. This result is in agreement to the XRD findings, where it shows the retaining of the structure after the exchanged.

Fig. 3 shows the IR spectra of the dehydrated exchanged zeolite samples at the OH stretching region. Bands that appeared in the samples are Si-OH-Al groups in the framework (3606.6 cm⁻¹), and the hydroxyl group that bonded with the extraframework aluminium (3668.4 cm⁻¹). A small band near 3780 cm⁻¹ is only observed in parent HBeta. This band is assigned to the isolated extra-framework AlOOH⁺ species. The vibration band at 3743 cm⁻¹ is assigned to the O – H stretching of silanol group [16-18]. The intensity of this band however decreases with the increase of the size of the cations exchanged. This suggests that besides the ion-exchange process which occurred at the oxygen vicinity of the alumina tetrahedral framework, some of the alkaline metals might have exchanged with the silanol defect sites and occluded at this sites, causing the decrease in the intensity of the silanol group.

Cs⁺ has the largest size compared to Na⁺ and K⁺ and most of the cations shows predominantly to occupy the defect sites rather than the normal ion-exchanged process of the narrow channels from the zeolite framework. This explained the missing band of the OH silanol group in CsBeta sample.

3.2 Basicity and acidity

Basicity and acidity properties were characterized by Temperature programmed desorption (TPD) to measure the number and strength of base and acid sites that available on the surface of a catalyst. A mild acidic CO₂ was used as probe for basicity and NH₃ for acidity. The strength and amount of base sites are reflected in the desorption temperature and the peak area, respectively, in a TPD plot.
The TPD-CO$_2$ thermograms of the exchanged zeolite beta is as shown in Fig. 4. One expects that by exchanging the protons with alkali metal with a lower electronegativity, the oxygen charge will increase and thus increase the basicity of the zeolite. However, the results show no increment of the basic strength in zeolite beta after exchange with sodium, potassium and cesium compared to the parent H-Beta. As shown in Fig. 4, the broad peaks at 240°C and 390°C for HBeta, 350°C for NaBeta, 330°C for KBeta and 390°C for CsBeta were observed. It reveals that the trend of the basic strength of HBeta, NaBeta, KBeta and CsBeta does not follow the trend of the size and the electropositive character of alkali metal cations (Na$^+ < K^+ < Cs^+$). The basic strength also does not follow the trend of the relative crystallinity (see Tab. 1). CsBeta is supposed to create the highest the basic strength. However, it shows that its basic strength is similar to those the parent H-Beta.

Tab. 1 gives the number of base sites counted from TPD-CO$_2$. From TPD results it was observed that the amount of base sites among the samples was different. Compared to HBeta, the concentration of base sites in NaBeta and KBeta is significantly higher. It also reveals that the concentration of base sites in CsBeta and Hbeta are about the same. Theoretically, the basicity must be affected by the strength and the amount of the base sites. In order to show that the base strength and the amount of the base sites affect the basicity, the Sanderson electronegativity equivalence method (SEEM) [9] is adapted. The SEEM can determine the negative charge carried by the oxygen in zeolite frameworks. The intermediate electronegativity $S_{int}$ of a given material reflects the mean electronegativity reached by all the atoms as a result of electron transfer during formation of the compound. For a compound $P_{p}Q_{q}R_{r}$, the intermediate electronegativity $S_{int}$ is given by,

$$S_{int} = \left( \frac{S_{p}}{S_{p}^2 + S_{q}^2 + S_{r}^2} \right)^{1/2}$$

(1)

where the composition of the catalyst is $P_{p}Q_{q}R_{r}$, $S$ is the elemental electronegativity, and $S_{int}$ is the intermediate electronegativity. The electronegativity gives access to the negative partial charge on the oxygen atom in the framework by,

$$\delta_0 = \frac{S_{int} - S_0}{2.08/\sqrt{S_0}}$$

(2)

The oxygen charge of the ion-exchanged zeolite beta that calculated based on SEEM are tabulated in Tab. 1. As shown in Tab. 1, it is found that the basicity of the HBeta, NaBeta and KBeta is correlated with their oxygen charge. Thus, the basicity of zeolite beta is depending on the amount of sodium and potassium that has been exchanged in the zeolite beta framework. On contrary, cesium exchanged zeolite beta has lower basicity even though the calculated oxygen charge is the highest among all the samples. This might due to the cesium cations are located at the silanol defect sites which is corresponded to the peak around 3740 cm$^{-1}$ in Fig. 3 [16]. This argument is supported by the fact that the silanol defect sites band in the IR hydroxyl group study is disappear (Fig. 3). Since the base strength is also dependent on the structure, it should be noted that the basicity is also affected by the crystallinity of the CsBeta. One considers that the lower the crystallinity, the higher is the amount of the silanol defect sites. It confirms that if the crystallinity is taking into account, as shown in Tab. 1, the value of the oxygen charge ($-\delta_0$ times relative crystallinity) which is related to the basicity is become low. Therefore, the low basicity that due to the occupancy of cesium at defect site in CsBeta is correlated with the oxygen charge.

The acidity was also measured with TPD by using NH$_3$ as probe. The TPD-NH$_3$ thermograms that obtained are as shown in Fig. 5. The acidity of zeolite beta decrease significantly after exchanging with alkali metal cations in the order of $H^+ > Na^+ > K^+ > Cs^+$. By exchanging the proton in zeolite beta framework with alkali metal cations, the crystallinity of the...
samples decrease and the amorphization become obvious in the order of $H^+ < Na^+ < K^+ < Cs^+$. In crystalline structure, the framework is in the maximize resonance. The Si-O bond is strengthened, thus weaken the O-H bond. As a result, the interaction between proton and the framework structure become weaker such that the acid property increases. On the other hand, the resonance is weaker in the amorphous structure causing the decrease in acid properties compared to the crystalline structure [20]. It then explains the significant decrease in the acidity, i.e. about 4- and 5-fold in $KBeta$ and $CaBeta$, respectively than the parent $HBeta$.

Since the basicity of exchanged samples is insignificant, the decrease in the acidity is not due to the cation exchanged but rather to the crystallinity of the samples. A good correlation ($R^2 = 0.7631$) is found when the acidity is correlated against the relative crystallinity (Tab. 1). This suggests that the crystallinity affects the acidity in zeolite. In addition, as shown in Tab. 1, no correlation was observed between acidity and basicity. This suggests that the acidity and basicity properties of the ion-exchanged zeolite beta are independent.

4 CONCLUSION

The acidity and basicity properties of zeolite beta can be modified through ion exchange with alkali metal cations ($K^+$, $Na^+$ and $Cs^+$). The acidity property in zeolite beta reduces significantly after exchanged with a larger size of alkali cations with retaining the framework structure. The acidity of the ion-exchanged zeolite beta was decrease after ion exchange with $K^+$, $Na^+$ and $Cs^+$ cations as indicated by the amount of the NH$_3$ desorption in the TPD experiments. However, the acidity does not seem to depend on the type of alkali metal cations, but strongly depend on the crystallinity of the ion-exchanged beta zeolite. Furthermore, the basicity of the ion-exchanged zeolite beta is not significant, since the amount of the basic sites was always lower compared the acidity. It was found that the basicity was affected by both the crystallinity and the type of alkali metal cations.

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Sulfation: a simple method to enhance the catalytic activity of TS-1 in epoxidation of 1-octene with aqueous hydrogen peroxide

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Abstract
Titanosilicate (TS-1) has been successfully modified by sulfation to exhibit enhanced catalytic activity in the oxidation of 1-octene with aqueous \( \text{H}_2\text{O}_2 \). A high activity of the sulfated TS-1 was related to modifications of the local environment of Ti active site upon interaction with the \( \text{SO}_2^\text{+} / \text{CO}_2^\text{+} / \text{C}_211 \).  

Keywords: TS-1; Epoxidation; Sulfation; Enhancement of catalytic activity

1. Introduction
The discovery of the framework substituted microporous materials titanium silicalite-1 (TS-1) was one of the most important developments in heterogeneous catalysis with in the last decade [1]. These materials exhibit extremely high selectivity in oxidation reactions using hydrogen peroxide, with water as the major byproduct. Since there is a low concentration of Ti present in TS-1 the catalytically active Ti centers are believed to be site isolated from each other. This site isolation is thought to give rise to its unique catalytic activity and selectivity. It has been reported that the catalytic activity of TS-1 for olefin epoxidation with aqueous \( \text{H}_2\text{O}_2 \) could be enhanced by trimethylsilylation in order to produce hydrophobic TS-1 [2]. However, trimethylsilyl group can block the pore of the TS-1 since its size is considerably big. Here, we demonstrated a simple method to enhance the catalytic activity of TS-1 in epoxidation of 1-octene with aqueous \( \text{H}_2\text{O}_2 \) by sulfation. This simple method can eliminate the possibility of pore blockage.

2. Experimental
2.1. Synthesis
TS-1 (2% of Titanium, mol%) was prepared according to a procedure described earlier [1,3], using reagents, i.e., tetraethyl orthosilicates (Merck, 98%), tetraethyl orthotitanate (Merck, 95%) in isopropyl alcohol, tetrapropylammonium hydroxide (Merck, 20% TPAOH in water) and distilled water. The hydrothermal crystallization was carried out at 175 °C under static condition in the stainless steel autoclave for 4 days.

Sulfated TS-1 was prepared by impregnation method as follows: About 1 g of TS-1 was added into 25 ml of \( \text{H}_2\text{SO}_4 \) 0.5 M under vigorous stirring at 80 °C for 3 h. After evaporation of water, the solid was dried at 100 °C for 24 h. The solid sample was then calcined at 550 °C for 3 h. The sample was denoted as \( \text{SO}_4\text{/TS-1} \).
2.2. Characterizations

The solid structure was determined by using X-ray diffraction (XRD), infrared (IR) and UV–Vis Diffuse Reflectance (UV–Vis DR) spectroscopy techniques. All samples were characterized by powder XRD for the crystallinity and phase content of the solid materials using a Bruker Advance D8 Diffractometer with the Cu Kα (λ = 1.5405 Å) radiation as the diffracted monochromatic beam at 40 kV and 40 mA. The sample was scanned in the 2θ range between 5° and 50°. IR spectra of the samples were collected on a Perkin–Elmer Fourier Transform Infrared, with a spectral resolution of 2 cm−1, scans 10 s, at room temperature by KBr pellet method. The framework spectra were recorded in the region of 1400–400 cm−1. UV–Vis DR spectra were recorded under ambient conditions on a Perkin–Elmer Lambda 900 UV/Vis/NIR spectrometer. The acidity of the solids characterized by absorbed base probe molecule. The wafer of the sample (10–12 mg) was locked in the cell equipped with CaF2 windows, and evacuated at 400 °C under vacuum condition for 4 h. Pyridine as probe molecule was introduced into the evacuated sample at room temperature. IR spectra of the sample was monitored at room temperature after desorption of pyridine at 150 °C for 1 h.

2.3. Epoxidation of 1-octene

All reactions were carried out at room temperature with 1-octene (1.0 ml), 30% H2O2 (0.5 ml), a mixture of methanol (5 ml) and acetone (5 ml) as solvent, and catalyst (50 mg) with stirring. The products of reaction were analyzed by GC and GC–MS.

3. Results and discussion

XRD was used to characterize the structure and the crystallinity of the TS-1 and SO4/TS-1. All samples show similar XRD patterns characteristic of MFI structure type of zeolite. Introduction of SO42− anions into the TS-1 has no effect on the sample crystallinity, with less than 1% changes. This suggests that the MFI structure of TS-1 is still maintained after the introduction of SO42−. IR spectra of TS-1 and SO4/TS-1 samples show a peak at around 970 cm−1 which is a characteristic for titanium with tetrahedral structure (Fig. 1). This band appears to be diminished in the sulfated material, suggesting the decrease in the amount of tetrahedral titanium in SO4/TS-1. IR spectrum of SO4/TS-1 shows a new peak at around 1384 cm−1 which is corresponded to the asymmetric stretching vibration of the covalent S=O for SO42− ion.

Fig. 2 shows UV–Vis DR spectra of TS-1 and SO4/TS-1. The band in the range of 190–220 nm is attributed to a charge-transfer of the tetrahedral titanium sites between O2− and the central Ti(IV) atoms, while octahedral Ti is observed at around 310–330 nm [4,5]. It shows that, for TS-1, only single high intense band at around 208 nm can be observed. This band is attributable to titanium in the tetrahedral structure. Impregnation of SO42− into the TS-1 shows a medium intense band at around 215–228 nm and a shoulder band at around 270–312 nm, characteristic for titanium with tetra-
rahedral and octahedral structure, respectively. The peak intensity of tetrahedral titanium for \( \text{SO}_4/\text{TS-1} \) is lower than that of the parent sample (TS-1). The decrease in intensity of the tetrahedral titanium and the formation of the octahedral titanium indicate the occurrence of the transformation of some of the tetrahedral titanium framework to the octahedral structure or the extraframework during the sulfation. It has been calculated that 49% of tetrahedral titanium in the parent sample have been modified by sulfation.

As shown in Fig. 2, the wavelength of absorption band of the tetrahedral titanium sites (i.e., 288 nm) of \( \text{SO}_4/\text{TS-1} \) is higher than that of TS-1 (i.e., 208 nm). It could be that the Ti–O–S bonding in \( \text{SO}_4/\text{TS-1} \) lowered the charge-transfer excited state involving an electron transfer from \( \text{O}_2^+/\text{C}_0 \) to Ti

\[
\frac{1}{2} \text{Ti}^{n+} + \text{O}_2^+/\text{C}_0 \rightarrow \text{Ti}^{(n-1)+}/\text{C}_0 + \frac{1}{2} \text{hv}
\]

This phenomenon is supported by the fact that the band at 970 cm\(^{-1}\) of TS-1, which is corresponded to tetrahedral titanium, is shifted to higher wavenumber in \( \text{SO}_4/\text{TS-1} \) (see Fig. 1). The shift to higher wavenumber is expected since the presence of \( \text{SO}_4^2- \) species in \( \text{SO}_4/\text{TS-1} \) weakened the Ti–O–Si bonding, resulting in a longer bond length and hence decreasing the force constant of Ti–O–Si.

The acidity of the samples was characterized by pyridine adsorption. TS-1 and \( \text{SO}_4/\text{TS-1} \) only show the peak at around 1450 cm\(^{-1}\) (which is corresponded to Lewis acid site), while the peak at around 1545 cm\(^{-1}\) (which is corresponded to Brønsted acid site) was not observed (Fig. 3). This indicates that all samples only contain Lewis acid sites. It has been calculated that the amount of the Lewis acid sites in TS-1 and \( \text{SO}_4/\text{TS-1} \) were 12 and 8 \( \mu \)mol g\(^{-1}\), respectively, indicating a decrease of 33% in the Lewis acid concentration of \( \text{SO}_4/\text{TS-1} \) from the TS-1. This result suggests that the removal of tetrahedral titanium from the lattice to form octahedral species is the reason for the decrease in the acidity, since the amount of the Lewis acid sites correlate to the amount of tetrahedral titanium. No diol is observed in the reaction product of the epoxidation of 1-octene with aqueous \( \text{H}_2\text{O}_2 \) confirming that no Brønsted acid sites are present in the samples.

The infrared spectra of the TS-1 and \( \text{SO}_4/\text{TS-1} \) in the range of hydroxyl stretching regions at 4000–3000 cm\(^{-1}\) were recorded after evacuation in vacuum at 400 °C for 4 h (Fig. 4). TS-1 shows an intense band at 3736 cm\(^{-1}\) and a broad band at 3526 cm\(^{-1}\), characteristics for terminal silanol hydroxyl groups and hydroxyl groups with hydrogen bonding of water molecule with silanol groups, respectively [5]. The sulfation of TS-1 caused the sharp band of silanol groups to decrease significantly and becomes broader in the ranges of 3740–3726 cm\(^{-1}\), suggesting the formation of defect sites in the surface of TS-1. Meanwhile, the broad band for hydroxyl groups around 3500 cm\(^{-1}\) increases due to the hydroxyl groups are bounded on the sulfur centers.

As shown in Fig. 5, sulfation onto the surface of TS-1 increases its epoxidation activity. This phenomenon may be explained in terms of the local environment of Ti active site. It is generally accepted that isolated Ti(IV) are considered the most active species in epoxidation reaction. It has been found that tripod open lattice site
[i.e., Ti(OSi)OH] of Ti on the TS-1 surface was more active compared to the bipodal [i.e., Ti(OSi)2(OH)2] and the tetrapodal closed lattice sites [i.e., Ti(OSi)4][7,8]. Based on these findings, the effect of sulfation on increasing the epoxidation activity of SO4/TS-1 can be explained by the presence of tripodal Ti active site. As shown in Fig. 6, it proposes that the bipodal Ti reacted with SO2/C04 giving Ti(SiO)2SO4 and followed by the hydration of Ti(SiO)2SO4 resulting in the tripodal Ti site [i.e., Ti(OSi)2(SO3)OH].

The alternative explanation for the higher activity of SO4/TS-1 is that the formation of new sites generated by sulfation on the surface TS-1. The UV–Vis DR spectra shown in Fig. 2 clearly show that Ti has been removed from the lattice to form octahedral species. It is possible that it can migrate to the external surface. Since 1-octene is a relatively large molecule, one considers that an increase the number of external active sites and access on them could be a cause for the higher activity.

Based on the above considerations, the high activity of SO4/TS-1 for epoxidation of 1-octene by aqueous hydrogen peroxide can be considered as the influence of the attachment of SO42- to the Ti active sites or alternatively, the formation of new sites generated by sulfation in the surface TS-1.

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References

Fe(III)-salen encapsulated Al-MCM-41 as a catalyst in the polymerisation of bisphenol-A

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Abstract

Fe(III)-salen complexes encapsulated in the channels of Al-MCM-41 molecular sieves were successfully synthesised in situ by the flexible ligand method. The resulting compound was characterised by XRD, IR spectroscopy, nitrogen adsorption isotherm and 1H NMR techniques. The loading of complexes in Al-MCM-41 depends on the quantity of framework aluminium, suggesting that there is an electrostatic interaction between the positive charges of the encapsulated Fe(III)-salen complexes and the negative charges of the Al-MCM-41 framework. Polymerisation of bisphenol-A catalysed by Fe(III)-salen-Al-MCM-41 gave 67% conversion; significantly higher than the conventional homogeneous Fe(III)-salen catalyst.

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Keywords: Encapsulated Fe(III)-salen-Al-MCM-41; Zeozyme catalyst; Polymerisation; Bisphenol-A

1. Introduction

Metal complexes encapsulated into molecular sieves with suitable pore sizes such as zeolite Y, VPI-5 and mesoporous MCM-41 via covalent or ionic bonding, is expected to be as active as those present in metaloenzyme. Furthermore, the hybrid complex formed is structurally and thermally more stable, remain unchanged during reactions and gives higher conversions [1–3]. A number of metal complexes, for example Cu-phthalocyanine, Cu-salen, Cr-salen, Cu-pyridine, Mn-salen, Pd-salen and V-salen have been synthesised and encapsulated into molecular sieves such as zeolite Y [4–9].

Encapsulation of complexes into zeolite Y offers certain advantages whereby relatively large complexes (0.8 nm) cannot easily move in or out of the zeolite window (0.7 nm) which is smaller in size than the pores (1.2 nm). Unfortunately, reactions are only limited to small substrates since big substrates cannot enter the pores. In order to enable reactions involving bigger substrates, mesoporous MCM-41 having large pore size (2–5 nm) was used as an alternative. However the disadvantage of using MCM-41 as the host molecule is that the encapsulated active complex could easily be leached out. Because of this, some silicon atoms in the framework are substituted with aluminiums in order to induce ionic interactions between the positively charged metal complexes and the negatively charged framework aluminiums.

Although many studies have been reported on the synthesis of zeozymes or hybrid systems, Fe(III)-salen-Al-MCM-41 has not been reported. In this system, Fe(III)-salen complex acts as the guest with the active sites, whereas Al-MCM-41 as the host. Salen, \((N,N’\text{-bis(salicylidene)}\text{-ethylendiamine})\) being flexible in nature, enables it to easily penetrate the parallel channels of the hexagonal lattice structure of the mesoporous MCM-41. MCM-41 is also capable of protecting the active sites from detrimental reactions, preparing empty spaces for the substrates and active sites to react and directing the formation of bonds in a reaction.

This paper reports an in situ synthesis of Fe(III)-salen complex in the cavities of Al-MCM-41, by the flexible ligand method [10]. The physicochemical properties of the
so-called hybrid complex or zeozyme was characterised by X-ray diffraction (XRD), temperature programmed oxidation (TPO), infrared spectroscopy (IR), nitrogen adsorption isotherm and \(^1\)H NMR techniques. The catalytic activity of the Fe(III)-salen-Al-MCM-41 complex was studied in the oxidative polymerisation of bisphenol-A, using aqueous 30\% H\(_2\)O\(_2\) as the oxidant at room temperature.

2. Experimental

2.1. Synthesis of Fe(III)-salen-Al-MCM-41

Al-MCM-41 was synthesised directly using established technique [11]. The composition of the gel mixture was based on the ratio: \(x\) Al\(_2\)O\(_3\):6SiO\(_2\):HTABr:1.5Na\(_2\)O:0.15(N-H\(_4\))\(_2\)O:250H\(_2\)O with sodium aluminate (NaAlO\(_2\)) as the aluminium source. Four Al-MCM-41 samples with SiO\(_2\):Al\(_2\)O\(_3\) ratios of 40, 60 and 120 were synthesised following the gel composition listed in Table 1; labelled as AM-40, AM-60 and AM-120, respectively. Salen (\(X,N'\)-bis(salicylidene)-ethylenediamine) was synthesised by reaction of 1 mol ethylenediamine and 2 mol salicylaldehyde under reflux for 1 h. The yellow salen solid was washed with petroleum ether, dried and characterised. The synthesis of Fe(III)-salen (FS) complex was carried out by mixing 4.02 g (0.015 mmol) salen with 1 g (0.005 mol) iron trichloride anhydrate and Fe(III)-Al-MCM-41 (FSAM) was carried out by the flexible ligand technique. 0.007 mol salen was added to 5 g Fe(III)-salen-Al-MCM-41 to form Fe(III)-salen-Al-MCM-41 (FSAM) was carried out by the flexible ligand technique. 0.007 mol salen was added to 5 g Fe(III)-Al-MCM-41 and stirred at 150\°C in an oil bath for 3 h under a nitrogen gas flow. Excess Fe\(^{3+}\) ions in the solid were removed by ion exchange with 0.01 M NaCl solution and washing with hot water. Unreacted salen was removed by soxhlet extraction using dichloromethane until the colour of the extract disappeared. The calcined samples were characterised by XRD, FTIR and nitrogen adsorption.

2.2. Polymerisation of bisphenol-A

FSAM catalyst (100 mg) was reacted with bisphenol-A (5.0 mmol) in 10 mL dioxane with dropwise addition of aqueous 30\% H\(_2\)O\(_2\) for 3 h at room temperature. The product of the reaction was filtered in order to separate the catalyst from the solution and the filtrate was directly added into a 100 mL (50:50 v/v) methanol–water mixture. The solid product was centrifuged, dried and characterised. The same procedure was repeated for FS catalyst (3.8 mg).

2.3. Characterisations

Powdered X-ray diffraction (XRD) patterns of samples were recorded at 2\(\theta\) of 1.5\° to 10\° on a Siemens D5000 powder diffractometer with Cu-K\(_\alpha\) radiation at 35 kV and 35 mA. The BET surface areas and the pore size distributions were measured on a Micromeritics volumetric adsorption analyzer (ASAP 2010). Infrared spectra were recorded on Shimadzu 8000 spectrometer, using the KBr wafer technique. Fe(III)-salen-Al-MCM-41 (FSAM) sample; prepared as self-supporting wafer, was placed in a quartz cell equipped with CaF\(_2\) window, and heated in a tube furnace under vacuum (\(p = 1 \times 10^{-5}\) mbar) at 150\°C for 5 h. IR spectra of the cooled samples were recorded at the wavenumber range of 1700–1300 cm\(^{-1}\). Temperature programmed oxidation (TPO) data was obtained from Thermoquest TPDRO 1100. Samples were heated to 200\°C in a flow of nitrogen gas and analysed by flowing a gas mixture of 7.5\% oxygen in helium at a rate of 30 ml min\(^{-1}\) from 200 to 600\°C. \(^{29}\)Si MAS NMR spectra were recorded on a Bruker 400 MHz Avance at a frequency of 79.5 MHz, spinning at 5.5 kHz using 45\° pulses with a relaxation delay of 600 s. \(^{13}\)C and \(^{1}\)H MAS NMR spectra were recorded at a frequency of 100.6 and 399.9 MHz, spinning at 5 kHz using 1.9 \(\mu\)s pulses at 2 s relaxation time delays.

3. Results and discussion

X-ray diffractograms of SiMCM-41 and H-Al-MCM-41 samples with various SiO\(_2\):Al\(_2\)O\(_3\) ratios (AM-40, AM-60 and AM-120) in Fig. 1 consist of up to four reflections typical of hexagonal lattice structure of mesoporous MCM-41; indexed as (100), (110), (200), (210), respectively [13]. The appearance of intense peaks reflects the high degree of long range order of the samples. The peaks were broadened and shifted to higher angles with increase in the aluminium content. This means that the interplanar distance increases or there is an increase of the pore diameter of the AlMCM-41 (Fig. 1) since the ionic size of Si\(^{4+}\) (0.41 Å) ions are smaller than the Al\(^{3+}\) (0.53 Å) ions, which results in shorter Si–O bonds (1.61 Å), compared to Al–O bonds 1.75 Å [14]. Fe(III)-salen-Al-MCM-41 complex was brown in colour. The intensities of peaks in the X-ray diffractograms of Al-MCM-41 samples (Fig. 2) do not show much difference before and after encapsulation of Fe(III)-salen, indicating that the structure of Al-MCM-41 was not affected and remained intact throughout the process. There is a general shift of the peaks towards lower angles for MCM-41 samples having larger aluminium content; suggesting contraction of the pore diameter implying the formation of Fe(III)-salen complex.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al(_2)O(_3)</th>
<th>SiO(_2)</th>
<th>CTA(_2)O</th>
<th>Na(_2)O</th>
<th>(NH(_4))(_2)O</th>
<th>H(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM-40</td>
<td>0.15</td>
<td>6</td>
<td>1</td>
<td>1.5</td>
<td>0.15</td>
<td>250</td>
</tr>
<tr>
<td>AM-60</td>
<td>0.10</td>
<td>6</td>
<td>1</td>
<td>1.5</td>
<td>0.15</td>
<td>250</td>
</tr>
<tr>
<td>AM-120</td>
<td>0.05</td>
<td>6</td>
<td>1</td>
<td>1.5</td>
<td>0.15</td>
<td>250</td>
</tr>
</tbody>
</table>
The encapsulation of Fe(III)-salen was further confirmed by X-ray diffraction measurement and infrared spectroscopy (Table 2). Fig. 3 shows the IR spectra of samples FAM-60, FSAM-60, FS and salen after being heated in vacuum at 150°C. The peaks associated with the CH$_2$-N bonds of the salen complex are observed at 1700–1300 cm$^{-1}$ region of the IR spectrum. As expected, sample FAM-60 does not show any peaks in this region. Samples FSAM-60, FS and salen display similar peaks with some variations in position and intensities. There is a general shift of the peaks towards lower wavenumbers for samples FS and FSAM-60 with respect to salen due to two reasons. First, Fe cations are not in a free condition as in Fe-salen complex, instead they are bonded to the Al-MCM-41 framework as a charge neutralizer. Second, the Fe-salen being encapsulated in the channel of Al-MCM-41 restrict the movement of the complex due to lack of space. The presence of similar peaks indicates that Fe(III)-salen complex has been successfully encapsulated into the Al-MCM-41 framework. There was no substantial leaching of the complex since sample FSAM was exposed to soxhlet extraction with dichloromethane for three days.

Quantitative analysis on Fe(III)-salen in Al-MCM-41 (FSAM) with various SiO$_2$:Al$_2$O$_3$ ratios by IR given in Table 2 generally indicates that a larger quantity of Fe(III)-salen complexes are encapsulated into the Al-MCM-41 framework with lower SiO$_2$:Al$_2$O$_3$ ratios. Therefore, the loading of Fe(III)-salen complexes in Al-MCM-41 is dependent on the quantity of framework aluminium incorporated in MCM-41. The positive charges from the Fe(III)-salen complexes interact electrostatically with the negative charges of the framework Al, causing them to be strongly

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO$_2$/Al$_2$O$_3$</th>
<th>Pore diameter (nm)</th>
<th>Fe/Al-MCM-41 (wt/wt%)</th>
<th>CH$_2$-N peak area of complexes at 1602 cm$^{-1}$ stretching (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSAM-120$^b$</td>
<td>120</td>
<td>3.29</td>
<td>0.62</td>
<td>600</td>
</tr>
<tr>
<td>FSAM-60$^b$</td>
<td>60</td>
<td>3.42</td>
<td>0.91</td>
<td>900</td>
</tr>
<tr>
<td>FSAM-40$^b$</td>
<td>40</td>
<td>3.46</td>
<td>1.23</td>
<td>1600</td>
</tr>
<tr>
<td>FAM-60$^b$</td>
<td>60</td>
<td>3.67</td>
<td>1.27</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$ Analysed by FTIR.  
$^b$ Heterogeneous catalysis.  
$^c$ Analysed by XRD.
bonded to the framework and prevent them from being leached out.

The nitrogen adsorption studies of samples FAM-60 and FSAM-60 (Table 3) indicate a decrease in the surface area, pore volume and pore diameter by 31%, 25% and 21%, respectively; further confirms the encapsulation of salen into Fe(III)-Al-MCM-41. The percentage of iron in FSAM is lower than in FAM by about 30%. The reduction suggests that during encapsulation of salen, only iron that became part of the FSAM complex remained unleached in the system.

TPO profiles of samples FSAM with various SiO$_2$:Al$_2$O$_3$ ratios in Fig. 4 indicate the presence of peaks of various intensities at 325–400 °C region. The absence of the peak in sample FAM suggests that iron is present as Fe$_2$O$_3$. Whereas the presence of peaks in the region indicates that the amount of gas produced as a result of oxidation of sample is higher than the amount of oxygen needed for the reaction. Quantitative analysis indicates that an increase in the SiO$_2$:Al$_2$O$_3$ ratio of the Al-MCM-41 shows a decrease in the intensity of peak due to lower organic content of the gas produced; implying less Fe-salen complex being formed. This results further supports prior observation that a higher amount of salen is encapsulated into the framework with more aluminium.

The diagrammatic representation of the steps involved in the formation of Fe(III)-salen-Al-MCM-41 zeozyme complex is as follows:

The catalytic reactivity of FSAM zeozyme complex was tested in the polymerisation of bisphenol-A with hydrogen peroxide as the oxidising agent and dioxane as the solvent. The test results (Table 4) indicate that the higher the loading of iron complexes, the higher is the conversion of bisphenol-A, with a maximum of 66.7% produced by sample FSAM-40; significantly higher than that produced by homogeneous Fe(III)-salen catalyst. Although the functional groups in bisphenol-A and polybisphenol-A are the same,
Table 4
Catalytic tests on polymerisation of bisphenol-Aa

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Quantity of polybisphenol-A (g)</th>
<th>Percentage of reacted bisphenol-A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(III)-salen (FS)</td>
<td>0.22</td>
<td>19.3</td>
</tr>
<tr>
<td>FSAM-40</td>
<td>0.76</td>
<td>66.7</td>
</tr>
<tr>
<td>FSAM-60</td>
<td>0.71</td>
<td>62.3</td>
</tr>
<tr>
<td>FSAM-120</td>
<td>0.38</td>
<td>33.3</td>
</tr>
</tbody>
</table>

a All reactions were carried out at room temperature for 3 h: 100 mg catalyst; 5 mmol bisphenol-A; 3.4 mL 30% H2O2; 10 mL dioxane.

Table 5
Physical properties of bisphenol-A and polybisphenol-A

<table>
<thead>
<tr>
<th>Property</th>
<th>Bisphenol-A</th>
<th>Polybisphenol-A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>White</td>
<td>Brown</td>
</tr>
<tr>
<td>Melting point</td>
<td>153°C</td>
<td>300–320°C</td>
</tr>
<tr>
<td>Solubility (methanol–water)</td>
<td>Soluble</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>

Fig. 5. 1H NMR spectra of bisphenol-A and polymerisation product polybisphenol-A.

these materials can be distinguished from their physical properties which are significantly different as listed in Table 5. The activity of the catalyst remained unaffected after it was recycled twice but was found to decrease by more than 50% after the third recycle.

Fig. 5 shows the 1H NMR spectra of bisphenol-A and the polybisphenol-A produced from various catalytic reactions. Generally, all spectra show four similar peaks: δ = 0.8 ppm for methyl; δ = 5.8–6 ppm for aromatic proton in the ortho position, δ = 6.2–6.4 ppm for aromatic proton at meta position and δ = 7.2 for OH groups [15]. The peak at δ = 1.3 and 2 ppm are for acetone. However the spectra for polybisphenol consist of broader peaks due to the presence of more chemically inequivalent environment; typical of polymeric molecules.

Polymerisation of bisphenol-A is an oxidative polymerisation process. By using zeozyme complexes, the amount of polymer produced is much higher due to the hydrophilic nature of Al-MCM-41 which supports the adsorption of bisphenol-A towards the formation of phenoxy radicals. Bisphenol-A is then oxidised by the oxidant H2O2 catalysed by Fe(III)-salen-Al-MCM-41 to form the phenoxy radicals. The last stage of polymerisation is the combination of the radicals to form polybisphenol-A chains.

4. Conclusion
Fe(III)-salen-Al-MCM-41 has been successfully synthesised by the flexible ligand method. The quantity of Fe(III)-salen complexes encapsulated into Al-MCM-41 to form the zeozyme complex is related to the quantity of aluminium in the framework via an electrostatic interaction between the positively charged encapsulated complexes and negatively charged Al-MCM-41 framework. Encapsulation of the Fe(III)-salen into the pore of Al-MCM-41 is supported by a decrease in the pore volume and surface area of the host system. Fe(III)-salen-Al-MCM-41 zeozyme was an active catalyst for polymerisation of bisphenol-A with 100% selectivity and 67% conversion. The decrease in surface area of the catalyst complex supports that the oxidation of bisphenol-A occurred on the active sites of Fe(III)-salen encapsulated in the pores rather than those adsorbed on the external surface of the Al-MCM-41 host molecular sieves.

Acknowledgement
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References
Titanium Doped Octahedral Manganese Oxide Hybrid Catalyst in the Oxidation of Cyclohexene

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Abstract—Octahedral manganese oxide molecular sieves (OMS-2) was doped with titanium to form hybrid catalyst (Ti-OMS-2) by precipitation method. Atomic absorption and X-ray diffraction analysis indicate the incorporation of titanium into the framework of OMS-2. Infrared and pyridine adsorption measurements demonstrated that Lewis acid sites were created by the presence of titanium in the OMS-2. Ti-OMS-2 is the most active catalyst for the oxidation of cyclohexene with tert-butylhydroperoxide (TBHP) compared to titanium oxide (TiO₂) and OMS-2; suggesting a synergetic effect between Ti and OMS-2 in the hybrid catalyst.


Keywords: Octahedral manganese oxide, titanium oxide, oxidation, hybrid catalyst
1. Introduction

Heterogeneously catalyzed oxidation of olefins has been widely applied in numerous chemical, biological and pharmaceutical industries. Besides oxidation of olefins in liquid phases with molecular oxygen, aqueous or organic hydrogen peroxide in particular, has been of interest in recent years. Aqueous hydrogen peroxide is an efficient and environmentally friendly oxidant; since water or alkyl alcohol is the only by-product obtained as the result of its application in such reaction. Products of selective oxidation of olefins are important starting materials toward the production of many other fine chemicals and polymers [1].

The unique catalytic activity and selectivity demonstrated by titanium silicalite-1 (TS-1) in photocatalytic decomposition of halogen compound and oxidation of alkenes, reported recently [2], have generated much interest to probe the potential of titanium incorporated catalysts.

Octahedral manganese oxide molecular sieves (OMS-2) is currently considered as one of the most potential catalyst in the oxidation of alcohols and olefins [1,3,4]. Similar to zeolite molecular sieves, OMS-2 materials are manganese oxide (MnO₃; x = 1.85-2.00) of molecular dimensions. The framework structure of OMS-2 consists of 2 x 2 type tunnels; built up of MnO₆ octahedra with pore diameter of 46 Å [5]. Unlike other manganese oxide materials, OMS-2 molecular sieves can be easily synthesized. In addition, OMS-2 uniquely catalyzes liquid phase oxidation of alcohols with molecular oxygen via the Mars van Krevelen mechanism to selectively generate the desired product[3]. It is therefore desirable to study the catalytic performance of OMS-2 material with the addition or incorporation of suitable metal such as titanium.

This paper reports on the study of titanium doped OMS-2 (Ti-OMS-2) as hybrid catalyst in the oxidation of cyclohexene with tert-butyl hydroperoxide (TBHP) as the oxidant. The physical properties of OMS-2 and Ti-OMS-2 were characterized and their catalytic activity tested. The effect of incorporation of Ti on the catalytic activity of OMS-2 material was also studied.

2. Experimental

Catalyst Preparation

OMS-2 molecular sieves was prepared by precipitation method. 225 mL of 0.4M solution of KMnO₄ was added to 87.5 mL of 1.75M solution of MnSO₄·H₂O and 6.8 mL concentrated HNO₃ (Merck) followed by vigorous stirring. The mixture was then refluxed at 373 K for 24 h. The resulting black precipitate was filtered, washed and dried at 393 K. Ti-OMS-2 was prepared following the same procedure and conditions as in (i) where, 225 mL of 0.4M solution of KMnO₄ was added to 150 mL of 15 v/v% solution of Ti₂SO₄ in H₂SO₄ instead of MnSO₄ and HNO₃ solution.

Characterization of samples

X-ray diffraction analysis of the samples were performed using powdered X-ray diffractometer (Bruker D8 Advance) with Cu Kα radiation (λ = 0.1542 nm at 40kV and 40 mA), step size of 0.02° per minute and a scan rate of 10 s/step. The XRD patterns were recorded at 2θ of 5°-70°.

Infrared spectra were measured using a Perkin Elmer Fourier Transformed Infrared (FTIR) spectrometer with a spectral resolution of 4 cm⁻¹, 10 s scan time, 20°C temperature using the KBr pellet technique. The IR spectra were recorded in the wavelength region of 400 cm⁻¹-1400 cm⁻¹.

Acidity study was performed using the pyridine adsorption technique. 12 mg of the sample was pressed under 5 tonnes pressure for 10 s to form a 13 mm self-supporting wafers. The sample wafers were then placed in the IR cell with calcium fluoride
window. The sample was heated at 400°C in vacuum for 4 h. The IR spectra were recorded at room temperature using Shimadzu 2000 FTIR spectrometer with 2 cm⁻¹ spectral resolution. The types of acid sites were determined using pyridine as the probe molecule. Pyridine was adsorbed at room temperature and desorbed at 150°C for one hour.

Elemental analysis was carried out using atomic absorption spectrometer (AAS). The samples were analyzed for Mn, Ti and K. The solid samples were prepared by hydrofluoric acid method. 50 mg of sample was placed in a Teflon vessel with 0.5 mL aqua regia (v/v HNO₃:HCl = 1:3), 3 mL of HF (48%) was added and the tightly sealed vessel was placed in an oven at 110°C for 1 h. After cooling, the products were quantitatively transferred to a 50 mL plastic beaker containing 2.8 g of H₂O₂. 10 mL of water was added followed by stirring until a clear solution was obtained. The solution was further diluted to 100 mL prior to elemental analysis.

Catalytic reaction

Oxidation of cyclohexene was carried out using tert-butyldihydroperoxide (TBHP) as the oxidant. Typically, the reaction mixture consists of catalyst (50 mg), cyclohexene substrate (10 mmol), TBHP (5 mmol), solvent (10 mL acetonitrile) and cyclooctane (0.5 mmol) as an internal standard. The mixture was placed in a round-bottomed flask with a reflux condenser. The assembly was performed under a semi-bath conditions for 2 h. Upon completion, the liquid products were separated from the solid catalyst by filtration and analyzed by gas chromatography (GC) using DB-1MS column fitted with FID.

3. Results and Discussion

Figure 1 shows the XRD patterns of OMS-2 and Ti-OMS-2. The reflections were matched to those of cryptomelane Q [6]; the natural counterpart of OMS-2 material. The results confirmed that both OMS-2 and Ti-OMS-2 materials consist of the cryptomelane structure: 2 x 2 tunnels with a pore size of 4.6 Å, composed of double chains of edge-sharing and corner-sharing MnO₆ octahedra as depicted in Figure 2. The more intense reflections for Ti-OMS-2 sample suggest that the hybrid material is of higher crystallinity than the pure OMS-2 material.
Titanium Doped Octahedral Managanese Oxide Hybrid Catalyst in the Oxidation of Cyclohexene

The lattice parameters (a and c) and cell volumes of OMS-2 and Ti-OMS-2 samples calculated from XRD data given in Table 1 are typical for materials having tetragonal structure. However, the increase in cell volume of Ti-OMS-2 material indicates that Ti has been incorporated into the framework of OMS-2. This is further supported by the elemental analysis by AAS given in Table 2. The lower amount of Mn in Ti-OMS-2 hybrid material than OMS-2 suggests that

Table 1. Lattice parameters (a and c) and cell volumes (V) OMS-2 and Ti-OMS-2 hybrid catalysts calculated from X-ray diffraction data.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Lattice parameters (a)</th>
<th>Lattice parameters (c)</th>
<th>V (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMS-2</td>
<td>9.741</td>
<td>2.859</td>
<td>271.29</td>
</tr>
<tr>
<td>Ti-OMS-2</td>
<td>9.827</td>
<td>2.871</td>
<td>277.20</td>
</tr>
</tbody>
</table>

\[ \frac{1}{a^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \]

\[ V = a^2 c \]

Table 2. Composition of manganese and Ti/Mn ratios in OMS-2 and Ti-OMS-2.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Mn (mg)</th>
<th>Ti/Mn</th>
<th>K/(Mn+Ti)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMS-2</td>
<td>22.40</td>
<td>0</td>
<td>0.05</td>
</tr>
<tr>
<td>Ti-OMS-2</td>
<td>13.38</td>
<td>2.43</td>
<td>0.02</td>
</tr>
</tbody>
</table>

* In 50 mg of catalyst.

Ti has been incorporated in the framework of the latter. A low K/(Ti + Mn) ratio in Ti-OMS-2 also indicates that potassium ions in OMS-2 material has been substituted by the titanium ions. IR spectra of OMS-2 and Ti-OMS-2 are shown in Figure 3. The spectra acquired in the wavenumber range of 400 cm⁻¹ - 800 cm⁻¹ of both samples show the presence of peaks typically attributed to Mn-O vibrations found in OMS-2 materials [7,8].

Figure 3. FTIR spectra of (a) Ti-OMS-2 and (b) OMS-2.

Figure 4. FTIR spectra of (a) Ti-OMS-2 and (b) OMS-2 after evacuation under vacuum at 400 °C for 4 h followed by pyridine adsorption at room temperature and evacuation at 150 °C for an hour in the pyridine regions.
However, for Ti-OMS-2 sample, the peaks are generally shifted to longer wavenumbers due to the bigger size of Ti. In addition the spectrum of Ti-OMS-2 in Figure 2(a) shows a small peak at 967 cm\(^{-1}\) and 1000 cm\(^{-1}\) - 1050 cm\(^{-1}\) assigned to tetrahedral Ti and Ti-O stretching in Ti-OMS-2 respectively [9].

IR spectrum of acidity study by pyridine adsorption after evacuation under vacuum at 400 °C and 150 °C in Figure 4(a) shows that Lewis acid sites are formed in Ti-OMS-2 hybrid material as indicated by the appearance of peaks at 1447 cm\(^{-1}\), 1489 cm\(^{-1}\) and 1604 cm\(^{-1}\). In contrast, no peaks are observed for OMS-2 sample in Figure 4(b). The absence of peaks at 1540 cm\(^{-1}\) confirms that Brønsted acid sites are not found in both samples.

Oxidation of cyclohexene using TBHP as the oxidant catalyzed by TiO\(_2\) (anatase phase), OMS-2 and Ti-OMS-2 were analysed by GC. The yield of 2-cyclohexenone, 2-cyclohexenol and cyclohexene oxide as the reaction products are shown in Figure 4. As indicated in Figure 4, the reaction catalyzed by Ti-OMS-2 produced the highest yield of 2-cyclohexenone. Furthermore, the distribution data of the

Table 3. Distribution of products of oxidation of cyclohexene with TiO\(_2\), OMS-2 and Ti-OMS-2 as catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion* (%)</th>
<th>TON for Ti</th>
<th>Selectivity* (%)</th>
<th>cyclohexene oxide</th>
<th>2-cyclohexen-1-ol</th>
<th>2-cyclohexen-1-one</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)</td>
<td>11</td>
<td>0.15</td>
<td>0</td>
<td>40</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>OMS-2</td>
<td>22</td>
<td>25</td>
<td>2</td>
<td>38</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Ti-OMS-2</td>
<td>38</td>
<td>32</td>
<td>2</td>
<td>26</td>
<td>72</td>
<td></td>
</tr>
</tbody>
</table>

* conversion (%) based on substrate = [1 - (concentration of substrate left after reaction/initial concentration of substrate)] \times 100
* Selectivity (%) of product A = (concentration of product A/total concentration of all product) \times 100

Figure 5. The yield of 2-cyclohexen-1-one, 2-cyclohexen-1-ol and cyclohexene oxide in the oxidation of cyclohexene using TiO\(_2\), OMS-2 and Ti-OMS-2 as catalysts.
Titanium Doped Octahedral Manganese Oxide Hybrid Catalyst in the Oxidation of Cyclohexene

oxidation products of cyclohexene in Table 3 evidently demonstrate that Ti-OMS-2 gives the best conversion (38%), highest turnover number (TON = 32%) and selectivity for 2-cyclohexenone (72%). The superior performance of Ti-OMS-2 hybrid material strongly suggests a synergetic effect of Ti and OMS-2 in Ti-OMS-2 catalyst. The explanation of such characteristic and its mechanism is currently being studied.

4. Conclusion

Titanium doped octahedral manganese oxide (Ti-OMS-2) was successfully synthesized by precipitation method using titanium sulphate as the source of Ti. The structure of Ti-OMS-2 is similar to cryptomelane. Ti-OMS-2 is highly active and selective toward the oxidation of cyclohexene to give 2-cyclohexenone as the main product. The existence of Ti in the tunnel and framework structure of OMS-2 materials induces a synergetic effect that enhances the catalytic activity of the resultant hybrid catalyst.

References

Hydrophobic-Hydrophilic Catalytic System
Phase-boundary catalysis: a new approach in alkene epoxidation with hydrogen peroxide by zeolite loaded with alkylsilane-covered titanium oxide

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An NaY zeolite, modified with partly alkylsilane-covered titanium oxide and located at the boundary between aqueous and organic phases (a phase-boundary catalyst), acts as a catalyst for alkene epoxidation without stirring or the addition of a co-solvent to drive liquid-liquid phase transfer.

Utilization of hydrogen peroxide \( (\text{H}_2\text{O}_2) \) as an oxidant for organic substrates has received much attention in recent years because of its environmental implications; it gives only water as a product in a wide range of oxidation reactions. Moreover, it is less expensive and more accessible than other oxidizing agents, such as organic peracids or hydroperoxides. However, \( \text{H}_2\text{O}_2 \) is generally supplied as an aqueous solution, and when the substrate to be oxidized is insoluble in water, it is necessary to add a co-solvent to obtain a homogeneous reaction mixture. 1–3 Here, we propose a novel integrated chemical system, which we have termed ‘phase-boundary catalysis’, using aqueous \( \text{H}_2\text{O}_2 \) for the oxidation of organic compounds without any co-solvent. For this system, a particulate zeolite catalyst has been designed and prepared in order to be placed at the phase boundary between aqueous \( \text{H}_2\text{O}_2 \) and an organic substrate. Several authors have reported a ‘triphase system’ in which the homogeneous modification of a particulate catalyst loaded with metal ions or their complexes as active sites induced or accelerated the oxidation of organic substrates with \( \text{H}_2\text{O}_2 \) in aqueous solution. 3–5 In such triphase systems, however, vigorous stirring, leading to sufficient mass transfer, is required to drive the reaction. However, our strategy is different from those previously reported because we aim at placing the bifunctional particles, containing both hydrophilic and hydrophobic regions, at the phase boundary in order to catalyze the epoxidation reaction without requiring an emulsion containing the catalyst by stirring.

Modified zeolite on which the external surface was partly covered with alkylsilane was prepared in two steps. First, titanium(IV) tetraisopropoxide \( [\text{Ti(OPr}_3)_4, \text{Wako Pure Chemical, } < 200 \text{ mesh}] \) was impregnated from benzene solution into NaY zeolite powder \( \text{[IRC-Z-YS 5, supplied by the Catalysis Society of Japan and] and heated at 383 K overnight to give sample W-Ti-NaY. 500 nmol of Ti was used per gram of NaY unless otherwise stated. In the second step, n-octadecyltrichlorosilane (OTS, Tokyo Kasei) in toluene was impregnated into the W-Ti-NaY powder containing water \( (0.5 \text{ cm}^3/\text{g per g of NaY}) \) and heated at 383 K overnight. Due to the hydrophilicity of the W-Ti-NaY surface, addition of a small amount of water \( (0.5 \text{ g per g of W-Ti-NaY}) \) led to aggregation owing to the capillary force of water between particles. Under these conditions, it is expected that only the outer surface of aggregates, in contact with the organic phase can be modified with OTS, and indeed almost all of the particles were located at the phase boundary when added to an immiscible water–organic solvent \( (\text{W/O}) \) mixture. The partly modified sample is denoted W/O-Ti-NaY. Fully modified Ti-NaY \( (\text{O-Ti-NaY}) \), prepared without the addition of water in the above second step, is readily suspended in an organic solvent as expected. At present, it is not clear whether the position of alkylsilane attachment is on the zeolite, on the Ti oxide (hydroxide), or on both.

In the water adsorption experiment at room temperature, it was observed that the adsorption capacity of modified zeolites \( (8 \text{ mmol g}^{-1} \text{ for both W/O-Ti-NaY and O-Ti-NaY}) \) was not greatly different from that of the parent NaY zeolite \( (11 \text{ mmol g}^{-1}) \), suggesting that alkylsilane modification did not block the pores of zeolites. This observation is in agreement with the finding reported by Singh and Dutta. 6

Oct-1-ene \( (\text{Kanto Chemical, 97%}) \) was purified by passing it through a column of basic alumina and was used as a substrate for epoxidation reaction. Typically, oct-1-ene \( (4 \text{ ml}) \), 30% \( \text{H}_2\text{O}_2 \) aqueous solution, and the mixture was vigorously stirred for 20 h at ambient temperature. As can be seen in Table 1, all of the modified zeolites showed activity for epoxidation of oct-1-ene to give 1,2-epoxyoctane. GC analyses (Shimadzu GC-14B) indicated that 1,2-epoxyoctane was the sole product, and other probable by-products, such as octanone, octan-1-ol, octan-2-ol or octane-1,2-diol, were not produced. NaY modified by Ti-species only \( (\text{W-Ti-NaY}) \) was hydrophilic in nature, and was suspended in water when added to a W/O mixture. W-Ti-NaY showed appreciable epoxidation ability only under vigorous stirring, i.e. in the W/O emulsion, but was negligibly active without stirring, as shown in Fig. 1. Modification of Ti-NaY by alkylsilane led to a significant rate enhancement. In particular, partial modification by alkylsilane \( (\text{W/O-Ti-NaY, entry 3}) \) led to better activity than full modification \( (\text{O-Ti-NaY, entry 4}) \). A reference experiment using non-porous silica \( (\text{Wako Pure Chemical, } < 200 \text{ mesh}) \) was also carried out. Silica was modified in a similar manner to that of W/O-Ti-NaY. The epoxidation result showed that the yield of 1,2-epoxyoctane was lowered ten-fold compared to W/O-Ti-NaY \( (\text{entry 8}) \), suggesting that the pores might be playing a role in the catalytic reaction.

**Table 1** Catalytic room-temperature epoxidation of oct-1-ene

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Epoxide yield (%mol)</th>
<th>TON for Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>W-Ti-NaY</td>
<td>2.5</td>
<td>0.1</td>
</tr>
<tr>
<td>3</td>
<td>O-Ti-NaY</td>
<td>24.7</td>
<td>1.1</td>
</tr>
<tr>
<td>4</td>
<td>O-Ti-NaY</td>
<td>5.9</td>
<td>0.2</td>
</tr>
<tr>
<td>5</td>
<td>Ox-Ti-NaY</td>
<td>0.1</td>
<td>0.7</td>
</tr>
<tr>
<td>6</td>
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<td>0.1</td>
<td>0.7</td>
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<tr>
<td>7</td>
<td>W/Ti-NaY</td>
<td>22.7</td>
<td>45.4</td>
</tr>
<tr>
<td>8</td>
<td>W/O-Ti-silica</td>
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* All reactions were carried out at room temperature for 20 h with oct-1-ene \( (4 \text{ ml}) \), 30% \( \text{H}_2\text{O}_2 \) \( (1 \text{ ml}) \) and catalyst \( (50 \text{ mg}) \) with vigorous stirring; the concentration of Ti and alkylsilane = 500 \text{ mmol g}^{-1} \. The aqueous phase of entry 3 after the reaction. The reaction was conducted for 9 h. The reaction was performed after washing and drying of the catalyst. \( < 200 \text{ mesh} \).

The recovered and dried W/O-Ti-NaY catalyst was reused in a fresh \( \text{W/O mixture and showed ca. 60% activity. To the remaining reaction mixture, without the catalyst, was added 30% \text{H}_2\text{O}_2 \) aqueous solution, and the mixture was vigorously stirred for 20 h at ambient temperature. As can be seen in Table 1, all of the modified zeolites showed activity for epoxidation of oct-1-ene to give 1,2-epoxyoctane. GC analyses (Shimadzu GC-14B) indicated that 1,2-epoxyoctane was the sole product, and other probable by-products, such as octanone, octan-1-ol, octan-2-ol or octane-1,2-diol, were not produced. NaY modified by Ti-species only \( (\text{W-Ti-NaY}) \) was hydrophilic in nature, and was suspended in water when added to a W/O mixture. W-Ti-NaY showed appreciable epoxidation ability only under vigorous stirring, i.e. in the W/O emulsion, but was negligibly active without stirring, as shown in Fig. 1. Modification of Ti-NaY by alkylsilane led to a significant rate enhancement. In particular, partial modification by alkylsilane \( (\text{W/O-Ti-NaY, entry 3}) \) led to better activity than full modification \( (\text{O-Ti-NaY, entry 4}) \). A reference experiment using non-porous silica \( (\text{Wako Pure Chemical, } < 200 \text{ mesh}) \) was also carried out. Silica was modified in a similar manner to that of W/O-Ti-NaY. The epoxidation result showed that the yield of 1,2-epoxyoctane was lowered ten-fold compared to W/O-Ti-NaY \( (\text{entry 8}) \), suggesting that the pores might be playing a role in the catalytic reaction.

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* All reactions were carried out at room temperature for 20 h with oct-1-ene \( (4 \text{ ml}) \), 30% \( \text{H}_2\text{O}_2 \) \( (1 \text{ ml}) \) and catalyst \( (50 \text{ mg}) \) with vigorous stirring; the concentration of Ti and alkylsilane = 500 \text{ mmol g}^{-1} \. The aqueous phase of entry 3 after the reaction. The reaction was conducted for 9 h. The reaction was performed after washing and drying of the catalyst. \( < 200 \text{ mesh} \).
stirred at ambient temperature. A negligible increase in the amount of epoxide could be seen. These facts suggest that epoxide formation occurs at the phase boundary, and not from any leached Ti species. Although the turnover number (TON), the molar ratio of the epoxide to the loaded Ti, was almost unity for the reaction with W/O-Ti-NaY (entry 3) for relatively larger Ti loading, W/O-Ti-NaY with a lower Ti concentration (10 \( \text{mol g}^{-1} \)) (entry 7) gave a TON of ca. 45, indicating catalytic action of the Ti species. Higher loading might induce aggregation leading to inner inactive sites. One of the most striking features of W/O-Ti-NaY is shown in Fig. 1; the partial alkylsilane modification not only enhanced the epoxidation but also changed the mode of reaction. As described above, W-Ti-NaY showed activity only under vigorous stirring, and a similar behavior was seen for the O-Ti-NaY system in which the epoxide yield under static conditions was almost half of that of the stirred reaction mixture. On the other hand, the activity of W/O-Ti-NaY was not dependent on the stirring rate, i.e. this catalyst does not require the formation of W/O emulsion, completely at variance with previously reported results for the ‘triphase system’.7 The amphiphilic nature of W/O-Ti-NaY, enabling it to sit just at the W/O phase boundary, may account for the constant activity. Therefore, the rate of this phase-boundary catalysis depends only on the apparent area of the W/O interphase. In fact, when a narrow-bore reaction tube was used to decrease the apparent interphase area, the activity was reduced, as expected (data not shown).

All of the results mentioned above seem consistent with the mechanism of phase-boundary catalysis; amphiphilic particles having active sites (Ti-species) lie at the W/O interphase to catalyze the chemical reaction. However, the apparent rate of epoxidation was much lower than those previously reported. One of the reasons for the low activity in our catalysis is the presence of few four-coordinate Ti species which are considered to be the most active species in olefin epoxidation.9 It should be noted that we used the Ti-loaded NaY zeolite as an easily available material and the catalyst and the reaction conditions have not been optimized. Further study for improvement of catalytic activity by generating four-coordinated Ti species in the catalytic system is now underway. Thus, we have shown a new concept of phase-boundary catalysis, that is applicable when amphiphilic particles, molecular assemblies, or films with adequate active sites are used, to a wide range of catalytic reactions.

H. N. thanks the Japan Society for the Promotion of Science (JSPS) for granting a Postdoctoral Fellowship. We are grateful to the Catalysis Society of Japan for the supply of zeolite samples. This research was partly supported by a Grant-in-Aid for Encouragement of Young Scientists (No. 99300) from Ministry of Education, Science, Sports and Culture, Japan. Dr Hisashi Semb (Nippon Shokubai) is acknowledged for his stimulating suggestions and discussion.

Notes and references

Phase-Boundary Catalysis of Alkene Epoxidation with Aqueous Hydrogen Peroxide Using Amphiphilic Zeolite Particles Loaded with Titanium Oxide

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Received April 30, 2001; revised August 10, 2001; accepted August 10, 2001

INTRODUCTION

Due to increasing demand for clean and environmentally benign technologies in chemical process engineering, much attention has recently been paid to the establishment of ecologically more acceptable catalytic processes, including removal of toxic and expensive reagents, minimization of by-product formations, and simplification of workup procedures (1). In liquid-phase epoxidation of olefins, for example, various transition metal complexes are used as homogeneous catalysts because they show high selectivity and activity. However, substitution of these homogeneous catalytic systems with heterogeneous systems is desirable because of the simplicity of catalyst and product isolation from the reaction mixture and because of the possibility of operating the reaction continuously in heterogeneous systems.

In order to realize a cleaner oxidation process in the liquid phase, the selection of oxidants is important. Hydrogen peroxide (H₂O₂) is one of the most promising oxidants for a clean oxidation process because it gives only water as a product in a wide range of oxidation reactions. Moreover, it is less expensive and more accessible than other oxidizing agents, such as organic peracids or hydroperoxides. Therefore, heterogeneous catalytic oxidation using aqueous H₂O₂ would be desirable. However, one of the major problems encountered in this system is insufficient transfer of substrate and/or reagent molecules between organic solvent and water phases. The addition of cosolvents, leading to a homogeneous solution and eliminating the liquid-liquid phase boundaries, has been a general strategy (2, 3). Alternatively, the reaction rate could be improved by vigorous stirring to increase the apparent interface area (4). However, the presence of a third component or cosolvent or the formation of an emulsion by stirring would make the workup procedure very tedious.

Recently, we have proposed a new approach, called phase-boundary catalysis (PBC), for catalyzing the liquid-liquid phase reaction by using a solid catalyst and H₂O₂ under cosolvent-free conditions (5). The concept is based on the idea that an amphiphilic catalyst particle can be placed...
at the liquid–liquid phase boundary in order to catalyze the reaction without the presence of a cosolvent and without the formation of an emulsion containing a catalyst by vigorous stirring. Actually, we have demonstrated that amphiphilic Ti-loaded NaY zeolite prepared by partial modification with alkylsilane successively catalyzes epoxidation of 1-octene in this system. To the best of our knowledge, no catalytic reactions in a solid catalyst–H$_2$O$_2$ system similar to the PBC concept have been reported up to now. Here, we show the details and the mechanism of PBC for alkene epoxidation.

**EXPERIMENTAL**

**Catalyst Preparation**

NaY zeolite (JRC-Z-Y5.5) powder was supplied as a reference catalyst from the Catalysis Society of Japan and used as obtained. Partially modified zeolite, whose external surface was partly covered with alkylsilane, was prepared in two steps. First, titanium(IV) tetra-2-propoxide (Ti(OPr)$_4$, Wako Pure Chemical) was impregnated from its benzene solution into NaY zeolite powder and heated at 383 K overnight. Here, this modified zeolite is called w-Ti–NaY. The molar amount of Ti was 500 μmol g$^{-1}$ of NaY, unless otherwise stated. In the second step, the w-Ti–NaY powder with water (50 wt%) was immersed in 10 cm$^3$ toluene containing 500 μmol of n-octadecylchlorosilane (ODS, ShinEtsu), and the suspension was shaken for ca. 5 min at room temperature. Then, the solid was collected by centrifugation and dried at 383 K overnight. Due to the hydrophilicity of the w-Ti–NaY surface, the addition of a small amount of water led to aggregation by the capillary force of water among particles (6). Under these conditions, it is expected that only the outer surface of aggregates, being in contact with the organic phase, could be modified with ODS. The partially modified sample was labeled w/o-Ti–NaY. A similar procedure was also carried out for amorphous silica with a primary particle size of 500 nm (Nissan Chemical Industries), and it was labeled as w/o-Ti–silica.

Fully modified Ti–NaY (w/o-Ti–NaY) was prepared by a procedure similar to that reported previously (7). ODS (500 μmol) was dissolved in a mixed solution of toluene (80 vol%) and CCl$_4$ (20 vol%). A dried sample of w-Ti–NaY (1 g) was added to the solution, and the mixture was stirred overnight at room temperature. A solid sample was collected by centrifugation, washed with CCl$_4$ and then ethanol, and dried at 383 K overnight.

Amorphous titanium oxide (TiO$_2$) was also prepared according to the previously reported method (8) and modified with ODS. To a Ti(OPr)$_4$, 8 g ethanol (40 cm$^3$) solution, an ethanol (30 cm$^3$)–water (30 cm$^3$) mixture was added dropwise with vigorous stirring. White TiO$_2$ precipitate was dried at 383 K overnight. The TiO$_2$ sample was partially modified with ODS (w/o-Ti) by the same method as that used for the w/o-Ti–NaY preparation.

**Reaction Conditions and Analytical Methods**

Epoxidation of straight-chain alkenes such as 1-pentene, 1-heptene, 1-octene, and 1-dodecene was carried out under several reaction conditions. Typically, alkene (4 cm$^3$), 30% aqueous H$_2$O$_2$ (1 cm$^3$, Wako), and catalyst powder (50 mg) were placed in a glass tube, and the reaction was performed with or without stirring for 20 h at room temperature. Except for 1-octene, all of the alkenes, purchased from Kanto Chemicals, were used as obtained. Because of the presence of an appreciable amount of impurities, 1-octene was purified by passing through a column of basic alumina (Merek). The reaction products were analyzed by gas chromatography (a Shimadzu GC-14B gas chromatograph equipped with a flame ionization detector and PEG1000 and TENAX TA60/80 columns).

**RESULTS AND DISCUSSION**

**Physical Properties**

Figure 1 shows the apparent distribution of modified Ti–NaY catalysts suspended in an aqueous H$_2$O$_2$ (30%)–1-octene mixture. Since the original unmodified NaY and the loaded titanium oxide species are hydrophilic and do not easily disperse in organic solvents, the w–Ti–NaY was dispersed well in the aqueous phase, as expected (Fig. 1a). On the other hand, o-Ti–NaY was dispersed very well in the organic 1-octene phase due to its hydrophobic nature of covering octadeetyl groups on the external surface of Ti–NaY (Fig. 1c). It is worth noting that, compared with these modified NaY catalysts, almost all of the w/o-Ti–NaY particles were located at the aqueous–organic phase boundary (Fig. 1b). The characteristic behavior of w/o-Ti–NaY is attributable to its amphiphilicity (i.e., each w/o-Ti–NaY particle has both hydrophilic and hydrophobic faces).

In the water adsorption experiment, it was observed that the adsorption capacity of ODS-modified NaY catalysts at ambient temperature (8 mmol g$^{-1}$ for both w/o-Ti–NaY and o-Ti–NaY) was not so different from that of the parent NaY zeolite (11 mmol g$^{-1}$), indicating that the structure and hydrophilic features of internal pores of these NaY particles were retained and that the hydrophobic alkyl chains did not block the entrance of zeolite pores. These results agree well with the findings reported by Singh and Dutta (7).

**Catalytic Properties for Epoxidation of 1-Octene**

Table 1 summarizes the yields of 1,2-epoxyoctane and turnover number (TON) per Ti atom in epoxidation of 1-octene with aqueous H$_2$O$_2$ by using several catalysts under the condition of stirring. All of the modified NaY catalysts
showed activity for epoxidation of 1-octene to give 1,2-epoxyoctane (entries 2–4), and the reaction did not occur without catalysts (entry 1). Gas chromatography analyses indicated that 1,2-epoxyoctane was the sole product, and other expected by-products, such as 2-octanone, 1-octanol, 2-octanol, or 1,2-octanediol, were not detected. Modification of Ti–NaY with hydrophobic alkyl groups led to a significant rate enhancement. In particular, a partly modified catalyst (w/o-Ti–NaY, entry 3) showed much higher activity than did a fully modified one (α-Ti–NaY, entry 4) in the reaction at room temperature. A considerable increase in epoxide yield was also observed when the temperature was increased to 353 K using w/o-Ti–NaY as a catalyst (entry 5).

TABLE 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Epoxide yield/μmol</th>
<th>TON for Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>0.1</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>w/Ti–NaY</td>
<td>2.5</td>
<td>0.1</td>
</tr>
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<td>3</td>
<td>w/o-Ti–NaY</td>
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<td>3.1</td>
</tr>
<tr>
<td>4</td>
<td>α-Ti–NaY</td>
<td>5.9</td>
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</tr>
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<td>5</td>
<td>w/o-Ti–NaY⁶</td>
<td>88.7</td>
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<td>6</td>
<td>w/o-Ti–NaY⁵</td>
<td>22.7</td>
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<td>w/o-Ti–NaY reused⁴</td>
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<td>8</td>
<td>Solution⁴</td>
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</tr>
<tr>
<td>9</td>
<td>w/o-Ti</td>
<td>25.9</td>
<td>—</td>
</tr>
<tr>
<td>10</td>
<td>w/o-Ti reused⁴</td>
<td>6.0</td>
<td>—</td>
</tr>
</tbody>
</table>

* All reactions were carried out at room temperature for 20 h with 1-octene (4 cm³), 30% H₂O₂ (1 cm³), and catalyst (50 mg) with vigorous stirring. The concentration of Ti and alkylamine was 50 μmol g⁻¹.

* The reaction temperature was 353 K with the catalyst of entry 3.

* The concentration of Ti was 10 μmol g⁻¹.

* The reaction was performed after the catalyst was washed with methanol and dried at 338 K for 4 h.

* The aqueous phase of entry 3 after the reaction. The reaction was conducted for 9 h.

The TON, the molar ratio of the epoxide to the loaded Ti, was almost unity for the reaction with w/o-Ti–NaY (entry 3) of relatively larger Ti loading. On the other hand, w/o-Ti–NaY with a lower Ti concentration (10 μmol g⁻¹, entry 6) gave a TON of ca. 45, indicating catalytic action of Ti species. The higher loading might induce aggregation to make inactive inner Ti species.

Although w/o-Ti–NaY showed higher catalytic activity in an aqueous–organic (W/O) mixture, it is not clear whether the observed reaction proceeds with Ti species loaded on NaY particles or with those leached in the reaction mixture. In order to exclude the latter possibility, the w/o-Ti–NaY catalyst recovered and dried after reaction for 20 h (entry 3) was reused in a fresh W/O mixture, and the remaining reaction mixture, without the catalyst, was vigorously stirred for 9 h with addition of 30% H₂O₂. The activity of recovered w/o-Ti–NaY was ca. 60% of that of the fresh w/o-Ti–NaY (entry 7), but a negligible increase in the molar amount of epoxide could be seen in the latter solution (entry 8). These facts suggest that the epoxidation was catalyzed by the w/o-Ti–NaY particles but not by the leached Ti species. A decrease in activity, similar to that seen in the recovered w/o-Ti–NaY, was observed when amorphous TiO₂ was modified with ODS (w/o-Ti) by a procedure similar to that used for the w/o-Ti–NaY preparation; the activities of the recovered and dried w/o-Ti were decreased to ca. 75% (entries 9 and 10). Therefore, the decrease in activity of recovered w/o-Ti–NaY was attributed to surface modification, such as detachment of the alkyl chains or modification of the titanium species, during the reaction and/or regeneration processes of the catalyst.

**Phase-Boundary Catalysis**

Figure 2 shows the effect of stirring on the yield of 1,2-epoxyoctane. The activity of w-Ti–NaY was appreciable
under the condition of vigorous stirring (i.e., in the W/O emulsion) but was negligible without stirring. Similar behavior was seen in the w/o Ti-NaY system in which the epoxidation yield under static conditions was almost half that of the stirred reaction mixture. On the other hand, the activity of w/o Ti-NaY was independent of the stirring rate (i.e., this catalyst did not require the formation of a W/O emulsion by stirring). This is one of the most striking characteristics of w/o Ti-NaY and is completely different from previously reported results for the cosolvent free "triphase system" (9-11).

Thus, when w/o Ti-NaY was added to the W/O mixture, it spontaneously lay at the phase boundary (see Fig. 1) and exhibited unusual catalytic properties without stirring. Therefore, it was thought that the rate of this phase-boundary catalysis depends on the apparent area of the W/O interphase. To prove this, the reaction was carried out using reaction tubes with different bore sizes. Figure 3 shows dependence of the initial rate of 1,2-epoxyoctane formation on apparent interphase area per unit weight of the catalyst (S/W in m² g⁻¹). Saturation of the initial rate was achieved at around 0.2 of S/W for all of the reactions with catalysts of different weights. These results clearly indicate that the reaction rate of the PBC system is determined by the area of the interphase where the catalyst particles lie. Therefore, the efficient and/or optimum amount of catalyst in this system can be controlled by the S/W ratio.

The above-mentioned results seem to be consistent with the mechanism of PBC based on the concept that amphiphilic catalyst particles, containing both hydrophilic and hydrophobic regions, are placed at the phase boundary to realize a continuous supply of H₂O₂ and organic substrates to the active sites on the particles without stirring. In the following sections, the advantageous features of the amphiphilic particles in various reaction conditions and/or systems are discussed.

Previous studies on selective oxidation reactions in conventional systems have shown that the use of a suitable cosolvent increases the concentration of olefin in aqueous H₂O₂ and improves mass transfer between aqueous and organic phases (4). Based on this idea, we prepared a homogeneous mixture containing 1-octene (8%), aqueous H₂O₂ (8%), and ethanol (84%) as a cosolvent to examine the catalytic activity of modified NaY catalysts under stirring and static conditions. Figure 4 shows the results.

Under these conditions, no phase boundary was found, and all the catalysts were precipitated. As expected, for all catalysts, there were negligible effects of stirring on the yield of 1,2-epoxyoctane. Another point worth noting is that w/o Ti-NaY showed the highest activity among these catalysts, as seen in the PBC conditions. This suggests that the amphiphilic nature of w/o Ti-NaY, having higher affinity for both H₂O₂ and 1-octene, would improve the rate of reaction between them.

FIG. 2. The yield of 1,2-epoxyoctane using variously modified NaY under stirring and static conditions.

FIG. 3. Dependence of the amount of w/o Ti-NaY catalyst particle occupied at an interphase on the initial rate of formation of 1,2-epoxyoctane.

FIG. 4. The yield of 1,2-epoxyoctane in the presence of cosolvent. All reactions were carried out at room temperature for 20 h: 50 mg catalyst; 4 cm³ of the mixture of 1-octene (8%), ethanol (84%), and 30% aqueous H₂O₂ (8%).
An amphiphilic catalyst could be used in a reversed \( w/o \) mixture by modified NaY catalysts suspended in an aqueous \( \text{H}_2\text{O}_2/\text{CCl}_4 \) (6% of 1-octene) mixture. Due to the relatively high specific gravity, the organic \( \text{CCl}_4 \) phase by below the aqueous phase (i.e., the placement of organic–aqueous phases was inverted when compared with the 1-octene/\( \text{H}_2\text{O} \) mixture). Under these conditions, hydrophilic \( w/\text{Ti–NaY} \) was dispersed in the upper part, the aqueous \( \text{H}_2\text{O}_2 \) phase, as expected. On the other hand, the behaviors of \( o/\text{Ti–NaY} \) and \( w/o/\text{Ti–NaY} \) were completely different from those in the previous 1-octene/\( \text{H}_2\text{O} \) system; \( o/\text{NaY} \) immediately settled on the bottom part, the \( \text{CCl}_4 \) phase, and \( w/o/\text{Ti–NaY} \) was dispersed in the \( \text{CCl}_4 \) phase. These differences in distribution are attributed to the balance of hydrophobility and density between the catalyst particles and the organic solvent. Detailed description of the characterization of these samples will be published elsewhere (12). The trend in activities of \( w/o/\text{Ti–NaY} \), \( o/\text{Ti–NaY} \), and \( w/\text{Ti–NaY} \) in the reversed system was similar to that observed in the 1-octene/aqueous \( \text{H}_2\text{O}_2 \) system, indicating that at the mesomeric level, the amphiphilic region on \( w/o/\text{Ti–NaY} \) particles could enhance the adsorption of the oxidant and the substrate to react at the active Ti sites.

**Extension of Substrates**

Table 2 summarizes the results of catalytic epoxidation by \( w/o/\text{Ti–NaY} \) at ambient temperature with various straight-chain alkenes under stirring or static conditions. For all the alkenes used as substrates, corresponding epoxides were obtained as main products. Under static conditions, the yields of 1,2-epoxypentane and 1,2-epoxyheptane were ca. three times higher than those of 1,2-epoxyoctane and 1,2-epoxydocodane. The relatively high hydrophobicity and high reactivity of small alkenes could account for the different yields. On the other hand, under the condition of vigorous stirring, 1-pentene and 1-hexene gave even lower yields of epoxides. Semiquantitative analyses revealed that by-products such as ketones (2-pentenal, 2-hexenal, 1-hexen-3-one, 2-pentanal, and 1-penten-3-one) and alcohols (corresponding to the reduced forms of the above ketones) are produced from these small alkenes, especially under the condition of vigorous stirring. Although no quantitative analysis has yet been performed due to the lack of authentic samples of these by-products, it is assumed that the total yield of epoxides is reduced by the mechanism of successive or parallel oxidation of alkenes under the condition of stirring. The PBC conditions seem preferable, to avoid an unexpected side reaction, since it allows the epoxidation to proceed without stirring.

**Effect of Support and Model of the Reaction**

The effect of support material on the PBC reactions was examined. Nonporous silica having a particle size almost the same as that of NaY zeolite (ca. 500 nm) was modified by a procedure similar to that used for the \( w/o/\text{Ti–NaY} \) preparation and used in reactions for epoxidation of 1-hexene, 1-octene, and 1-dodecene. As Fig. 6 shows, the modified NaY zeolite gave a higher yield of epoxides than did the silica-based catalysts, suggesting that the pores of the NaY particles are important.

As described above, \( w/o/\text{Ti–NaY} \), having affinity for both hydrophobic and hydrophilic compounds, effectively catalyzed alkene epoxidation by using \( \text{H}_2\text{O}_2 \) as an oxidant even though the reaction was carried out under static conditions (i.e., without stirring or addition of a cosolvent). In the epoxidation of relatively reactive substrates such as 1-pentene and 1-hexene, much higher yields of epoxide were obtained under static conditions. It was found that NaY, having a microporous structure with a relatively large surface area, was

**Table 2**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Condition</th>
<th>Epoxide yield/μmol</th>
<th>By-products⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-Pentene</td>
<td>Static</td>
<td>51.3</td>
<td>Ketone, alcohol, diesel⁵</td>
</tr>
<tr>
<td>2</td>
<td>1-Pentene</td>
<td>Stirring</td>
<td>17.0</td>
<td>Ketone, alcohol, diesel⁵</td>
</tr>
<tr>
<td>3</td>
<td>1-Hexene</td>
<td>Static</td>
<td>51.6</td>
<td>Ketones, alcohols, diesel⁵</td>
</tr>
<tr>
<td>4</td>
<td>1-Hexene</td>
<td>Stirring</td>
<td>16.3</td>
<td>Ketones, alcohols, diesel⁵</td>
</tr>
<tr>
<td>5</td>
<td>1-Octene</td>
<td>Static</td>
<td>27.0</td>
<td>None</td>
</tr>
<tr>
<td>6</td>
<td>1-Octene</td>
<td>Stirring</td>
<td>27.4</td>
<td>None</td>
</tr>
<tr>
<td>7</td>
<td>1-Dodecene</td>
<td>Static</td>
<td>17.7</td>
<td>None</td>
</tr>
<tr>
<td>8</td>
<td>1-Dodecene</td>
<td>Stirring</td>
<td>20.0</td>
<td>None</td>
</tr>
</tbody>
</table>

⁴ Reaction conditions are the same as those given for Table 1.
⁵ Analyzed by gas chromatography–mass spectrometry.

† 2-Pentenal.
‡ 1-Hexene-3-one, 4-methyl-1-pentene-3-one, 1-hexen-3-one, and 1-hepten-3-one.
§ 1-Hexene-3-one and 1-octene-3-one.
Hydrophobic-Hydrophilic Catalytic System

FIG. 6. Effects of catalyst support and substrate on the yield of the epoxides (1,2-epoxyhexane, 1,2-epoxyoctane, and 1,2-epoxydodecane) in the phase-boundary catalytic system.

Preferable as a support in this system compared with nonporous silica with a smaller surface area. Furthermore, it should be noted that distribution of alkylsilyl groups on the external surface of w/o-Ti–NaY has been clarified by using fluorescence microscopy; each w/o-Ti–NaY particle has both hydrophobic and hydrophilic surfaces, i.e., one side is covered with alkylsilyl groups and the other is kept covered with hydroxyl groups (silanols). Details for this fluorescence microscopic study will be published elsewhere (12). On the basis of these results, a model of the PBC system is proposed (see Fig. 7). Although there is no experimental evidence for distribution of the Ti species at present, they should be attached to the external surface of NaY, since the estimated molecular size of Ti(OPr)i(4 (ca. 1.5 nm), the source of Ti sites, is larger than the size of pore-entrance of NaY (ca. 0.17 nm). Thus, the modified particles are spontaneously located at the interface in a W/O mixture with the hydrophobic side facing the organic phase and the hydrophilic side facing the aqueous phase.

Consequently, active Ti sites on the NaY surface can be in contact with both organic substrates and aqueous H2O2. During the reaction at the Ti sites, due to the decrease in the concentration of substrates and H2O2 at the interphase, the concentration gradient of these reagents may appear in both organic and aqueous phases; this gradient may generate a driving force to supply these reagents from respective bulk solutions, thereby enabling the reaction to proceed efficiently without any enforced manipulation, such as stirring, in order to drive liquid–liquid mass transfer. In order to achieve this, the catalyst must satisfy the following requirements: (i) existence of active Ti sites at the liquid–liquid phase boundary, and (ii) continuous supply of both substrates and H2O2 through the hydrophobic and hydrophilic parts of the catalyst particles. Therefore, if the catalyst particles consist of nonporous materials, the number of active sites are limited and efficient PBC cannot be expected. The use of a microporous material as a support must increase the effective interphase area of the catalyst (i.e., increase the number of active sites), resulting in higher activity.

It is noted that the apparent rate of epoxidation in the present system was much slower than those previously reported (10, 11). The most likely reason for the lower activity is the presence of a smaller number of 4-coordinated Ti species, which is considered to be the real active species in olefin epoxidation reactions (13). In the present study, however, we employed a feasible process of Ti loading and did not optimize the yield of 4-coordinated Ti species in the preparation process. The impregnation of the titanium species used in this study also may induce aggregation to form titanium oxide, which is considered to decompose H2O2. Actually, it was observed that the molar amount of consumed H2O2 was ca. 1 mmol on w/o-Ti–NaY, while the epoxide yields were less than 100 μmol (Table 2); i.e., in the present system we obtained less than 10% efficiency of H2O2 utilization. Therefore, further studies on improvement and optimization of the activity of a phase-boundary catalyst are now underway in our laboratory.

CONCLUSIONS

The epoxidation reaction of alkene by partially alkylsilylated titanium-loaded zeolite with H2O2 has been demonstrated. Alkylsilylation can modify both the physical and catalytic properties of titanium-loaded zeolite. Partial covering with alkyl groups on the external surface of the zeolite catalyst gave amphiphilicity to the particles, enabling the location just at the W/O interphase of aqueous H2O2 and organic compounds to catalyze the epoxidation reaction. This PBC system is advantageous because of its simplicity; we have described efficient epoxidation reactions using the PBC system in this paper, and we are planning to apply the PBC system to other catalytic reactions, such as hydrolysis,
hydroxylation, and esterification, of water-immiscible organo-
glic compounds using water or reagents in their aqueous
solutions.

ACKNOWLEDGMENTS

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Direct Observation of Bimodal Amphiphilic Surface Structures of Zeolite Particles for a Novel Liquid–Liquid Phase Boundary Catalysis

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Amphiphilic NaY zeolite particles were prepared by a partial modification of the external surface of NaY with alkylsilyle groups. When the particles were added to a mixture of aqueous hydrogen peroxide and normal alkene, they were feasibly located just at the liquid–liquid phase boundary even without stirring. Fluorescence microscopic observation of these particles selectively modified with fluorescent dye revealed that each particle has a bimodal amphiphilic surface structure; one side of the external surface is hydrophilic and the other is hydrophobic.

In view of the current interest in establishment of environmentally benign and ecologically more acceptable chemical processes, there is an increasing emphasis on utilization of solid catalyst particles instead of the use of either stoichiometric reagents or homogeneous catalysts. Several solid catalysts, such as zeolites, supported oxides, and clays, have been extensively studied for the development of environmentally benign chemical processes by using their acid and base or oxidation catalytic properties. However, one of the major problems encountered in the use of solid catalysts is the difficulty of effective interaction between water-immiscible substrate(s) and catalyst particles owing to their hydrophilicity, which hinders the contact with hydrophobic compounds in the organic phase. Two strategies have been proposed so far to overcome this problem. One is the addition of cosolvents to eliminate the phase boundary between organic and water phases and to give a homogeneous solution, and the other is stirring of the reaction mixture vigorously to make an emulsion. These systems may increase the effective concentration of reactants on the catalyst surface and thus give successful results. At the same time, however, the enhanced contact of organic and water phases with the catalyst may induce the production of undesired byproducts and/or decomposition of product(s). Moreover, complicated workup procedures, such as separation of products from the solvent including unreacted reagents, are necessary.

Recently, we have found a novel method for partially modifying the external surface of zeolite particles with alkylsilyle groups. The particles could be placed at a liquid–liquid phase boundary between aqueous hydrogen peroxide and water-immiscible organic compounds and act as an efficient catalyst for epoxidation of 1-octene without stirring. The reaction system is thus named “phase-boundary catalysis (PBC).” In our previous paper, we briefly reported some of the phenomenological aspects of catalytic functions in PBC. However, the structures of catalyst particles governing their catalytic property had not been clarified. In the present study, therefore, we examined PBC and the structure of amphiphilic catalyst particles in more detail, focusing on clarification of the distribution of alkylsilyle groups on the external surface of particles by using fluorescence microscopy.

Experimental Section

Sodium zeolite Y (NaY) supplied by the Catalysis Society of Japan (JRC-Z—Y.S.5.) was used as model zeolite particles. Titanium oxide species, active sites for epoxidation, were loaded by impregnation as follows. Titanium(IV) tetra-2-propoxide (0.142 g, 500 µmol, Wako Pure Chemical) dissolved in 20 cm³ of benzene (dried with molecular sieve 4Å) was added to 1.0 g of NaY powder, and the suspension was stirred at room temperature in open air until the benzene was almost evaporated. Then the resulting powder was heated at 383 K overnight. Here, the as-prepared zeolite loaded with titanium oxide is called Ti-NaY. An amphiphilic zeolite whose external surface was partially covered with alkylsilyle groups was prepared as follows. To 1 g of Ti-NaY, 0.5 cm³ of water was added and the mixture was stirred by a spatula until the added water soaked into Ti-NaY particles uniformly. The thus-obtained NaY aggregates were suspended in 10 cm³ of toluene solution containing 500 µmol of octadecyltrichlorosilane (OTS, Tokyo Kasei Organic Chemical). After the mixture was shaken for ca. 5 min at room temperature, the suspension was centrifuged to remove unreacted OTS and washed with CCl₄ (50 cm³) and ethanol (50 cm³), and the precipitates were dried at 383 K overnight. The thus-prepared particles were labeled w/o-Ti-NaY.

A similar procedure was also carried out to prepare fully modified Ti-NaY (o-Ti-NaY) without addition of water in the above procedure for preparation of w/o-Ti-NaY particles. In a typical experiment, OTS (500 µmol) solved in a mixed solution (10 cm³) of toluene (80 vol %) and CCl₄ (20 vol %). A dried sample of Ti-NaY (1 g) was added to the solution, and the mixture was stirred overnight at room temperature. A solid sample was collected by centrifugation, washed with CCl₄ (50 cm³) and ethanol (50 cm³), and dried at 383 K overnight.

Epoxidation of normal alkene with hydrogen peroxide was performed as follows. The modified NaY particles (50 mg), normal alkenes (4 cm³), and 30% of aqueous H₂O₂ (1 cm³) were placed in a glass tube and reacted for 20 h at room temperature. In some experiments, the mixtures were stirred magnetically. 1-Hexene
and 1-dodecene (Kanto Chemical) were used without further purification. Due to the appreciable amount of impurities, 1-octene (Kanto Chemical) was purified with basic alumina (Merck) before use. Reaction products were analyzed by gas chromatography (Shimazu GC-14B, PEG 1000 or Tenax TA column, FID detector, N2 carrier).

For clarification of the surface structures of these particles by fluorescence microscopy, fluorescein isothiocyanate (FITC) was attached to the surfaces of these particles by the procedure shown in Scheme 1. First, to 1 g of NaY (unmodified, denoted as NaY, w/o-NaY, or o-NaY) without Ti loading, 500 \( \mu \text{mol} \) of aminopropytriethoxysilane (APTS, Shinetsu Chemical) dissolved in toluene (10 cm\(^3\)) was added. After the suspension was stirred for 1 h at room temperature, the particles were collected by centrifugation, washed with CCl\(_4\) (50 cm\(^3\)) and ethanol (50 cm\(^3\)), and dried at 383 K overnight. To these APTS-modified NaY particles (200 mg), ca. 0.1 mmol of FITC hydrochloride (Research Organics) in methanol (10 cm\(^3\)) was added and stirred at room temperature overnight. After separation of the particles by centrifugation, they were washed several times with 10 cm\(^3\) of methanol and dried at room temperature in the dark for 24 h. Removal of unreacted FITC from the particles was confirmed by its negligible absorption in the supernatant by UV–vis spectrometry (Hewlett-Packard HP8453).

Fluorescence microscopic observation was performed at room temperature using a fluorescence microscope (Olympus BHT-RFK) and a CCD camera (BITRAN BS-30L) with a “B filter” for excitation at 480 nm. The FITC-modified particles were dispersed in ethanol by ultrasonication for a few minutes. The upper part of the suspension was spread on a glass plate and used as a sample. We could observe the particles being ca. 10–40 \( \mu \text{m} \) in size, aggregates of crystallites (ca. 1 \( \mu \text{m} \)), with sufficient resolution to compare the difference between the samples.

### Results and Discussion

Figure 1 shows the apparent locations of Ti-NaY, w/o-Ti-NaY, and o-Ti-NaY suspended in a 1-octene–aqueous hydrogen peroxide (30%) mixture. Since an NaY particle itself and loaded titanium oxide species are originally hydrophilic owing to their surface hydroxyl groups, the Ti-NaY particles were only dispersed in the aqueous H\(_2\)O\(_2\) phase (Figure 1a). When the surface hydroxyl groups of Ti-NaY were modified with OTS, as has been extensively used for silica,9,10 these particles (o-Ti-NaY) became hydrophobic due to the surface coverage of alkylsilyl groups. As expected, o-Ti-NaY was only dispersed in 1-octene (Figure 1c). Similar behavior has been reported by Dutta et al.8 To adjust the surface coverage of alkylsilyl groups, a small amount of water, slightly more than the water-absorption capacity of Ti-NaY estimated by a separate experiment,11 was added to the dried Ti-NaY powder before the reaction with OTS. Since the capillary force of water induces tight adhesion

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(11) Water absorption capacity of Ti-NaY was measured at room temperature by a simple absorption technique. A 1 g portion of NaY dried at 573 K was exposed to air with high humidity (90–100%) at ambient pressure. After the exposure, the weight increase of the particles was recorded in several intervals and the saturated increase (ca. 30%) was assumed to be the absorption capacity.
aggregates. Therefore, the surface of w/o-Ti-NaY is
with hydroxyl groups existing on the outer parts of
OTS molecule into the aggregates, OTS can only react
the binding water prevents insertion of a hydrophobic
are to be presented elsewhere. Details of the catalytic function toward several alkenes
suppression of further oxidation and/or side reaction.
under the static condition was partly attributable to the
vealed appreciable liberation of byproducts such as ketone
gas chromatography–mass spectrometry (GC–MS) re-
the condition of stirring. A semiquantitative analysis by
condition was three times higher than that obtained under
substrate, the yield of 1,2-epoxyhexane under a static
stirring at ca. 1000 rpm. When 1-hexene was used as a
catalyst does not require the formation of an emulsion by
Ti-NaY was independent of the stirring rate; i.e., this
activity of w/o-Ti-NaY was much higher than those of Ti-
NaY and o-Ti-NaY. It is notable that the activity of w/o-
activity of w/o-Ti-NaY was much higher than those under the condition of vigorous stirring. The
of 1,2-epoxyhexane under a static condition was higher
substrate. Similar behavior was seen in the o-Ti-NaY
case. Ti-NaY showed lower activity than did the others,
responding epoxides were obtained as major products in all
alkenes. Ti-NaY showed lower activity than did the others,
the epoxide yield under a static condition was much
lower than that under the condition of vigorous stirring.
Notably, the reaction did not occur even under the condition of stirring when 1-dodecene was used as a
substrate. Similar behavior was seen in the o-Ti-NaY
system except for 1-hexene epoxidation in which the yield of 1,2-epoxyhexane under a static condition was higher than that under the condition of vigorous stirring. The
activity of w/o-Ti-NaY was much higher than those of Ti-
NaY and o-Ti-NaY. It is notable that the activity of w/o-
Ti-NaY was independent of the stirring rate; i.e., this
catalyst does not require the formation of an emulsion by
stirring at ca. 1000 rpm. When 1-hexene was used as a
substrate, the yield of 1,2-epoxyhexane under a static condition was three times higher than that obtained under the
condition of stirring. A semiquantitative analysis by
gas chromatography–mass spectrometry (GC–MS) re-
vealed appreciable liberation of byproducts such as ketone
(hexenal) and alcohol (hexenol) under the condition of
stirring. Therefore, the higher yield of 1,2-epoxyhexane
under the static condition was partly attributable to the
suppression of further oxidation and/or side reaction.
Details of the catalytic function toward several alkenes
are to be presented elsewhere.

Table 1 summarizes the results of epoxidation of normal alkene by Ti-NaY, o-Ti-NaY, and w/o-Ti-NaY. Corresponding epoxides were obtained as major products in all cases. Ti-NaY showed lower activity than did the others, and the epoxide yield under a static condition was much lower than that under the condition of vigorous stirring. Notably, the reaction did not occur even under the condition of stirring when 1-dodecene was used as a substrate. Similar behavior was seen in the o-Ti-NaY
system except for 1-hexene epoxidation in which the yield of 1,2-epoxyhexane under a static condition was higher than that under the condition of vigorous stirring. The
activity of w/o-Ti-NaY was much higher than those of Ti-
NaY and o-Ti-NaY. It is notable that the activity of w/o-
Ti-NaY was independent of the stirring rate; i.e., this
catalyst does not require the formation of an emulsion by
stirring at ca. 1000 rpm. When 1-hexene was used as a
substrate, the yield of 1,2-epoxyhexane under a static condition was three times higher than that obtained under the
condition of stirring. A semiquantitative analysis by
gas chromatography–mass spectrometry (GC–MS) re-
vealed appreciable liberation of byproducts such as ketone
(hexenal) and alcohol (hexenol) under the condition of
stirring. Therefore, the higher yield of 1,2-epoxyhexane
under the static condition was partly attributable to the
suppression of further oxidation and/or side reaction.
Details of the catalytic function toward several alkenes
are to be presented elsewhere.

Table 1. Room Temperature Epoxidation of Normal
Alkenes on Several Modified Ti-NaY with 30% Aqueous
Hydrogen Peroxide

<table>
<thead>
<tr>
<th>alkene</th>
<th>Ti-NaY</th>
<th>w/o-TiNaY</th>
<th>o-NaY</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>stirring</td>
<td>static</td>
<td>stirring</td>
</tr>
<tr>
<td>1-hexene</td>
<td>4.5</td>
<td>0</td>
<td>16.2</td>
</tr>
<tr>
<td>1-octene</td>
<td>2.5</td>
<td>0.2</td>
<td>27.4</td>
</tr>
<tr>
<td>1-dodecene</td>
<td>0</td>
<td>0</td>
<td>20.0</td>
</tr>
</tbody>
</table>

* All reactions were carried out for 20 h with normal alkenes (4 mL), 30% H₂O₂ (1 mL), and catalyst (50 mg). The concentration of Ti was 500 mmol g⁻¹. ¹ Yields of corresponding 1,2-epoxide of alkenes.

between the particles, leading to aggregation, and since
the binding water prevents insertion of a hydrophobic
OTS molecule into the aggregates, OTS can only react
with hydroxyl groups existing on the outer parts of aggregates. Therefore, the surface of w/o-Ti-NaY is
expected to be bimodal, having both hydroxyl and alkylsilyl faces. Upon dispersion of w/o-Ti-NaY in the 1-octene–
30% aqueous H₂O₂ mixture, the particles were assembled
at the liquid–liquid phase boundary (Figure 1b). Similar
behavior was also observed when w/o-Ti-NaY was added to
several mixtures of aqueous (water)/organic (oil) solu-
tion. The characteristic behavior of w/o-Ti-NaY particles
is attributed to their appropriate balance of hydrophilicity
and hydrophobicity. We have confirmed the reproducibility
of preparation of the amphiphilic particles.

Figure 2. Fluorescence and optical micrographs of fluorescent dye-modified NaY particles: (a) FD-NaY, (b) FD–w/o-NaY. Outlines are shown for comparison.

On the basis of the above results, the characteristic
behavior of w/o-Ti-NaY particles, e.g., their feasible
location at the liquid–liquid phase boundary and the
remarkable catalytic ability of the particles for epoxidation
of normal alkenes, are attributed to the amphiphilic
feature of each particle, i.e., each w/o-Ti-NaY particle has
both hydrophilic and hydrophobic faces. To prove this, we
tried to determine the distribution of hydroxyl groups on
w/o-Ti-NaY particles by fluorescence microscopy. The
procedure to make the original nonfluorescent NaY surface
fluorescent consisted of two steps: aminoalkylation of
hydroxyl groups on the bare surface and then attachment
of fluorescent dye molecules through the amide linkage.
As a result, the whole external surface of unmodified NaY
and a (hydrophilic) part of the w/o-NaY surface without
attached alkylsilyl groups might be covered with the dye
molecules (Scheme 1a,b). On the other hand, due to the

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14) The external surfaces of aggregates were not wetted apparently though the amount of added water was larger than the estimated water-
absorption capacity of Ti-NaY. When more than 1 cm₃ of water was added in a 1 g portion of dried Ti-NaY particles, aggregates becomes
sticky and, as expected, the resulting alkylsilylated particles seemed heterogeneous; some particles were located in the liquid–liquid phase
boundary and others were dispersed in water.

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full surface coverage with hydrophobic alkylsilyl groups on o-NaY, APTS cannot react with its surface to retain inertness of the surface to FITC. Thus, the fluorescent dye molecules were expected to be attached only on the hydrophobic surface, i.e., the external surface of o-NaY; o-NaY could not be fluorescent (Scheme 1c). UV–visible diffuse reflectance spectroscopy revealed that FD–NaY has strong absorption and FD–w/o-NaY has less-intense absorption at about 400–550 nm, while o-NaY treated with APTS and FITC gave no absorption in this region (data not shown). These facts agree with the above-mentioned expectation, and we could therefore exclude the possibility of existence of physically adsorbed fluorescent dye species.

Figure 2 shows representative fluorescence and optical microscopic images of FD–NaY and FD–w/o-NaY. For FD–NaY particles, there was no appreciable difference in shape (as shown by outlines in Figure 2) between fluorescence and optical images; i.e., aminopropylsilyl groups and fluorescent dye molecules were grafted on the whole external surface (Figure 2a), as expected. On the other hand, in the case of FD–w/o-NaY, only a part of the particles was fluorescent (Figure 2b). These findings confirmed that hydroxyl groups on w/o-NaY were exposed on only one side of the external surface and the remainder of the external surface was covered with alkylsilyl groups, hindering the reaction with APTS and FITC; i.e., each particle of w/o-NaY has both a hydrophilic and a hydrophobic surface. It should be noted that some of w/o-NaY particles gave either fluorescence on the whole surface or negligible fluorescence. It is thus reasonable to assume that partially alkylsilylated particles with different orientations existed on a sample glass plate.

Thus, we have clarified the amphiphilic surface structure of the modified NaY particles used in PBC systems, one side being hydrophilic and the other hydrophobic. It is reasonable to assume that during the reaction in PBC, the w/o-NaY particles are spontaneously located at the liquid–liquid phase boundary in an aqueous–organic mixture, facing the hydrophobic alkylsilylated surface to the organic phase and the hydrophilic side to the aqueous phase. In this situation, both normal alkenes and H₂O₂ in the aqueous phase can be continuously supplied through the hydrophobic and hydrophilic surfaces of w/o-Ti-NaY. As shown in Figure 1c, some of the o-Ti-NaY particles seem to be situated at the liquid–liquid phase boundary due to gravity. Actually, all of them became assembled at the phase boundary after standing for a few hours. Similar behavior was also observed for H-ZSM5 modified by several silane coupling reagents suspended in an aqueous (water)/organic (oil) mixture. However, because of the lack of hydrophilic sites (surfaces) for supplying H₂O₂, o-Ti-NaY showed much lower activity than that of w/o-Ti-NaY. This is consistent with the PBC mechanism mentioned above.

Although we could only observe relatively larger (ca. >10 µm) particles in the present study due to the limitation of resolution of fluorescence microscopy, we believe that the basic concept of amphiphilic catalyst particles driving the reaction at the liquid–liquid phase boundary has been proved. The apparent rate of epoxidation was lower than that previously reported. Therefore, to design a more efficient catalyst particle in PBC, structural analyses in the nanometer-to-micrometer region, e.g., more detailed analyses of the surface structure of amphiphilic particles, local structure, and distribution of loaded titanium species, are now underway.

Acknowledgment. The authors are grateful to the Catalysis Society of Japan for supplying zeolite samples. This research was partly supported by a Grant-in-Aid for Encouragement of Young Scientists (No. 13750753) from the Japan Society for the Promotion of Science (JSPS). H.N. thanks the JSPS for financial support.

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Effect of Titanium Active Site Location on Activity of Phase Boundary Catalyst Particles for Alkene Epoxidation with Aqueous Hydrogen Peroxide

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Abstract
Epoxidation of 1-octene with hydrogen peroxide at room temperature was examined using bimodal zeolite particles, in which some of the external surfaces some were covered with hydrophobic alkyl groups and the rest were left hydrophilic. When bimodal titanium-loaded NaY were added to a mixture of aqueous hydrogen peroxide and 1-octene, these particles could be assembled just at the liquid-liquid phase boundary, resulting in the formation of a particulate film, and efficiently catalyzed the epoxidation of 1-octene even without agitation. On the other hand, when TS-1 particles in which the active titanium species located mainly inside the pore system were used, there were no significant effects of partial modification on catalytic activity under the conditions of both stirring and no stirring. These results suggested that titanium species located on the external surfaces of particles were dominantly effective for the observed phase boundary catalytic system.

1. INTRODUCTION

There has been an increasing demand for the development of environmentally benign and ecologically more-acceptable methods for production of organic fine chemicals. Substitution of chemical reaction systems with stoichiometric reagents by heterogeneous catalytic reaction systems is desirable because of the simplicity of isolation of a catalyst(s) and product(s) from the reaction mixture and because of the possibility of operating the reaction continuously [1]. A major problem in the use of heterogeneous catalysis is the difficulty of effective interaction between a water-immiscible substrate(s) and catalyst particles owing to their hydrophilicity, which hinders the contact with hydrophobic compounds in the organic phase. Recently, we have devel-
opined a novel method for partial modification of the external surfaces of zeolite particles with alkylsilyl groups [2-4]. The particles could be assembled at a liquid-liquid phase boundary between aqueous hydrogen peroxide and water-immiscible organic compounds and act as an efficient catalyst for epoxidation of 1-octene without stirring or addition of a co-solvent. The reaction system has thus been named phase boundary catalysis (PBC). In the present study, we show some of new findings of PBC for alkene epoxidation to clarify the effective location of active titanium (Ti) sites in the catalyst.

2. EXPERIMENTAL

NaY zeolite (JRC-Z-Y5.5) was supplied as a reference catalyst from the Catalysis Society of Japan and used as received. Titanium(IV) tetra-2-propoxide (Ti(OPr)_4, 500 µmol) dissolved in 20 cm³ of benzene was added to 1.0 g of NaY, and the suspension was stirred at room temperature in open air until the benzene had almost completely evaporated. The resulting powder was then heated at 383 K overnight (w-Ti-NaY). Crystalline microporous titanium silicate, TS-1, was prepared according to the previously described procedure [5] and was designated w-TS-1. Bimodal particles partially covered with alkylsilyl groups on their external surfaces were prepared as follows (Fig. 1). To 1 g of w-Ti-NaY or w-TS-1, 0.5 cm³ of water to be absorbed by the particles was added, and the mixture was stirred until the added water soaked uniformly into the particles. The thus-obtained w-Ti-NaY or w-TS-1 aggregates were suspended in a toluene solution containing 500 µmol of octadecyl-trichlorosilane (ODS). After shaking the mixtures for ca. 5 min at room temperature, the suspensions were centrifuged to remove unreacted ODS, and the precipitates were dried at 383 K overnight. The as-prepared particles were labeled w/o-Ti-NaY and w/o-TS-1, respectively. Alkylsilyl-covered Ti-NaY and TS-1 catalysts without addition of water before the ODS treatment were also prepared and labeled o-Ti-NaY and o-TS-1, respectively. Epoxidation of 1-octene with hydrogen peroxide was performed as follows. The modified catalysts (50 mg), 1-octene (4 cm³), and 30% of aqueous H₂O₂ (1 cm³) were placed in a glass tube and reacted for 20 h at room temperature. In some experiments, the mixtures were stirred magnetically. Reaction products were analyzed by GC equipped with a DB-1 column and an FID detector.
3. RESULTS AND DISCUSSION

Table 1 summarizes the yields of 1,2-epoxyoctane and turnover number (TON) per Ti atom in epoxidation of 1-octene with aqueous \( \text{H}_2\text{O}_2 \) using unmodified and modified Ti-NaY at room temperature. When the reaction was operated under the condition of vigorous stirring, all of the modified NaY catalysts showed activity for epoxidation of 1-octene to give 1,2-epoxyoctane. Small amounts of expected by-products, such as 1-octanol or 1,2-octanediol, were also detected. The catalyst partly covered with alkylsilyl groups (w/o-Ti-NaY) showed highest activity among the catalysts examined. Under the condition of no stirring, w-Ti-NaY showed almost no activity; the epoxide yield was much lower than that obtained under the condition of vigorous stirring. Similar behavior was seen in the o-Ti-NaY system. On the other hand, it is notable that the activity of w/o-Ti-NaY seemed independent of the stirring rate, i.e., this catalyst does not require the formation of a W/O emulsion by stirring. This characteristic behavior of w/o-Ti-NaY particles might be attributed to the bimodal feature of each particle, i.e., each w/o-Ti-NaY particle has both hydrophilic and hydrophobic faces that induce affinity for both hydrophobic and hydrophilic compounds and continuous supply of reagents from both organic and aqueous phases without any enforced manipulation such as stirring in order to drive liquid-liquid mass transfer [3,4].

Figure 2 shows the results of epoxidation of 1-octene at room temperature on TS-1 systems. As was observed in the Ti-NaY system, 1,2-epoxyoctane was obtained as the main product with small amounts of other by-products. However, the order of catalytic activity was completely different from the Ti-NaY system; the highest activity was observed on unmodified TS-1 (w-TS-1), and modification with ODS induced a decrease in activity under the condition of stirring. Moreover, under the condition of no stirring, partial modification with alkylsilyl groups on the external surfaces of TS-1 particles to give the particles a bimodal character only slightly improved the activity compared with that of hydrophobic o-TS-1 particles being almost fully covered with alkylsilyl groups on the external surfaces.

Since the estimated molecular size of Ti(OPr)\(_4\) (ca. 1.5 nm) is larger than the size of the pore entrance of NaY (0.7 nm), Ti species should attach to the external surfaces of NaY particles.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>epoxide yield / ( \mu \text{mol} )</th>
<th>TON per Ti atom</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>stirring</td>
<td>no stirring</td>
</tr>
<tr>
<td>w-Ti-NaY</td>
<td>2.5</td>
<td>0.5</td>
</tr>
<tr>
<td>w/o-Ti-NaY</td>
<td>27.4</td>
<td>27.0</td>
</tr>
<tr>
<td>o-Ti-NaY</td>
<td>5.9</td>
<td>3.0</td>
</tr>
</tbody>
</table>

All reactions were carried out for 20 h with 1-octene (4 cm\(^3\)) and catalyst (50 mg). The concentration of Ti was 500 \( \mu \text{mol} \) per one gram of NaY.
The alkylsilyl groups are attached to one side of the external surfaces of NaY particles, giving the particles a bimodal character. Thus, the hydrophilic-hydrophobic balance of active Ti sites on the external surfaces of NaY particles is thought to be controlled by the surface modification. On the other hand, in TS-1 catalysts, due to the predominant location of active Ti sites in the pore system, the surface modification might be ineffective for changing their environments. Moreover, the relatively hydrophobic character of the original TS-1 particles, which enable them to adsorb sufficient amounts of organic reagents [6], might also account for the lack of a significant effect of coverage of alkylsilyl groups on catalytic activity.

The bimodal Ti-NaY particles (w/o-Ti-NaY, Table 1) showed less than half of the activity of the original TS-1 particles (Fig. 2). One of the most probable reasons for this is the difference in the nature of active sites of Ti species, i.e., the presence of a small number of 4-coordinated Ti species, which are considered to be the active species in olefin epoxidation reactions [7,8]. Only almost unity of TON (Table 1) also suggests the presence of large amounts of aggregates that are inactive for the reaction. However, we employed a feasible process of Ti loading and did not optimize the yield of 4-coordinated Ti species in the preparation process. Further studies to clarify and control the structure of loaded Ti species for improvement and optimization of the catalytic activity of PBC are now underway.

References
AMPHIPHILIC NaY ZEOLITE PARTICLES LOADED WITH NIOBIC ACID: MATERIALS WITH APPLICATIONS FOR CATALYSIS IN IMMISCIBLE LIQUID-LIQUID SYSTEM

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Abstract

The catalytic potential of catalysts for acid-catalyzed reactions has been demonstrated by NaY zeolite loaded with alkylsilane-covered niobic acid in the liquid phase hydration of 1,2-epoxyoctane with water. The catalytic activity of the catalysts was correlated to the amphiphilic character of the solid catalyst particles.

Keywords: Amphiphilic zeolite particles, acid-catalyzed reactions

INTRODUCTION

The fast-growing insight into green chemistry has led to research more focused on the area of environmentally benign catalysts [1, 2]. Along this line, we recently reported a new approach to modify the surface of zeolite, resulting hydrophilic and hydrophobic regions, for application as catalyst in immiscible liquid-liquid systems in co-solvent free condition [3-6]. The organic transformations under solvent-free conditions are attracting increasing attention because the use of large quantities of organic solvents is not only

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detrital to the environment but also economically unfavorable. The proposed model of a catalyst for immiscible liquid-liquid reactions is depicted in Fig. 1. Previously, we reported a zeolite loaded with alkylsilane-covered titanium oxide as catalyst for the oxidation of alkenes using aqueous H$_2$O$_2$. In this paper, the study is now extended to acid catalysis in which the hydration of 1,2-epoxyoctane using NaY zeolite loaded with niobic acid-covered alkylsilane is chosen as a model catalytic system. It has been reported that the surface acid strength of niobic acid (Nb$_2$O$_5$·nH$_2$O) corresponds to the acid strength of 70% sulfuric acid and exhibits high stability for acid catalyzed reactions in which water molecules participate [7]. Here, we demonstrate that the catalytic activity of the modified zeolite can be attributed to the amphiphilic character of the solid particles.

![Fig. 1. Proposed model of catalyst for immiscible liquid-liquid reactions](image)

**EXPERIMENTAL**

NaY zeolite (JRC-Z-Y5.5) with a primary particle diameter quoted as ca. 500 nm was supplied by the Catalysis Society of Japan and used as received. NaY zeolite loaded with niobic acid (Nb-NaY) was prepared by impregnation of niobium pentaethoxide (Nb(OC$_2$H$_5$)$_5$) from its ethanol solution at room
temperature. Then, the solid was heated at 130°C overnight. The molar amount of Nb was 500 µmol g⁻¹ zeolite. Unmodified Nb-NaY is labeled as w-Nb-NaY. Modified Nb-NaY, on which the external surface was covered partly with alkylsilane, was prepared by attachment of n-octadecyltrichlorosilane (ODS). This preparation method is similar to those given in our recent papers [3-6]. In a typical experiment, in order to modify w-Nb-NaY with alkylsilane, the w-Nb-NaY powder containing water (0.5 g per 1.0 g of w-Nb-NaY) was immersed in 5 mL of toluene containing 500 µmol of n-octadecyltrichlorosilane (ODS, ShinEtsu) and the suspension was shaken for ca. 5 min at room temperature. Then the solid was collected by centrifuging and dried at 110°C for 5 h. Due to the hydrophilicity of the w-Nb-NaY surface, addition of a small amount of water led to aggregation owing to the capillary force of water between particles. Under these conditions, it is expected that only the outer surface of aggregates which, is in contact with the organic phase can be modified with ODS. The partly modified sample was labeled as w/o-Nb-NaY. Fully modified Nb-NaY (o-Nb-NaY) was prepared without addition of water.

Hydration of 1,2-epoxyoctane with water was carried out at 70°C. In detail, 1,2-epoxyoctane (1 mL), water (1 mL) and catalyst powder (25 mg) were placed in a glass tube, and the reaction was performed at 70°C with stirring (ca. 1000 rpm) after removal of oxygen by argon bubbling. The reaction products were analyzed by gas chromatography (Shimadzu GC-14B with FID and DB-1 column) and GC/MS.

The photograph of the emulsion formed in the presence of modified NaY zeolite particles was taken under an optical microscope. Before the photograph was taken, the mixture was stirred vigorously at ca. 1000 rpm. Methylene blue (dissolved in aqueous phase) was used as an indicator in order to clarify the type of the emulsion, either oil in water (o/w) or water in oil (w/o).

RESULTS AND DISCUSSION

Figure 2 shows the rate of the formation of 1,2-octanediol in the mixture of 1,2-epoxyoctane and water in the presence of modified Nb-NaY catalysts. It confirms that the hydration of epoxyoctane is more efficiently catalyzed by w/o-Nb-NaY than both w-Nb-NaY and o-Nb-NaY. In order to rationalize the activities in hydration of 1,2-epoxyoctane, one should consider the formation of emulsion, because in this form the specific interfacial interactions between the solid catalyst surface and the two immiscible liquid phases increase the surface contact (wettability) of the catalyst with the reactants. For maximum efficiency, the catalyst should be wetted preferentially by the two liquid phases. If the solid particles are too strongly wetted by either of the two liquid phases
the required stabilizing action will not result [8]. Based on these considerations, the formation of the emulsion in the presence of the solid particles was examined. It was observed that, after ca. 30 min of reaction, an emulsion was formed in the system containing w/o-Nb-NaY, whereas o-Nb-NaY was still located at the organic phase due to its hydrophobic nature. Instead, w-Nb-NaY was distinctly well dispersed in the aqueous phase. After ca. 10 h of reaction, an emulsion was also formed in the system containing o-Nb-NaY. As is shown in Fig. 3, it is clearly demonstrated that an emulsion has been formed, resulting in an abrupt visual homogenization. No emulsion was formed in the system containing w-Nb-NaY.

If the surface structure of w/o-Nb-NaY has a good hydrophile-lipophile balance, one expects that the two immiscible liquids can be stabilized for a long period of time. Figure 4 shows the optical microscope photographs of the type of emulsion formed; the w/o-Nb-NaY and o-Nb-NaY act as emulsifier to
stabilize the 1,2-epoxyoctane and water mixture in the form of w/o type of emulsion. Interestingly, the emulsion can be stabilized by w/o-Nb-NaY for up to 24 h, whereas stability of emulsion for the system containing o-Nb-NaY was only 1 hour. This suggests that w/o-Nb-NaY possesses a good bimodal amphiphilic character to stabilize the immiscible mixture of organic and aqueous phases in order to form a relatively more stable emulsion.

All the systems containing modified niobic acid functionalized zeolites (w-Nb-NaY, w/o-Nb-NaY and o-Nb-NaY) produced 1,2-octanediol as the major product (Fig. 2). The w/o-Nb-NaY gave the highest yield of diol compared to those of w-Nb-NaY and o-Nb-NaY. It is possible that the hydrophilic and hydrophobic regions of w/o-Nb-NaY play an important role in the eventual formation of the diol by supplying continuously the organic and aqueous substrates to the active sites.
Although experimental evidence is not yet available at this stage, the Nb active sites and alkylsilyl groups should be attached to the external surface of NaY since the estimated molecular size of Nb(OCH₃)₅ (ca. 0.90 nm), the source of Nb sites, and alkylsilane (ca. 0.5 nm x 2.6 nm), the source of alkylsilyl, are larger than the size of the pore-entrance of NaY (ca. 0.70 nm). Based on these data, there is a possibility of the alkysilyl being attached to the
niobic acid sites, leading to a decrease in the activity of o-Nb-NaY. In order to exclude this argument, the Temperature Programmed Desorption (TPD) of preadsorbed ammonia measurements were performed on w-Nb-NaY, w/o-Nb-NaY and o-Nb-NaY. It was observed that no significant difference in the strength and amount of acid sites from the calculated amount of desorbed ammonia among the samples (data not shown). This suggests that the acid sites on the modified samples are not covered by ODS. On the basis of these results, it can be proposed that the higher activity of w/o-Nb-NaY is due to the stabilization of liquid-liquid system by bimodal amphiphilic particles as shown in Fig. 4a.

In conclusion, the results described above indicate that w/o-Nb-NaY (NaY zeolite loaded with alkylsilane-covered niobic acid) is potentially capable of catalyzing the hydration of 1,2-epoxyoctane at the interphase. The good catalytic activity could be related to the amphiphilic character of the solid particles.

REFERENCES

Phase-Boundary Catalysts for Acid-Catalyzed Reactions: The Role of Bimodal Amphiphilic Structure and Location of Active Sites

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O potencial catalítico para reações de interface de fases em reações catalisadas por ácidos foi demonstrado pelo zeólito NaY enriquecido com ácido nióbico recoberto por alquilsilano na reação de hidratação do 1,2-epoxioctano com água em fase líquida. O catalisador foi preparado através da impregnação do ácido nióbico na superfície externa de NaY, seguida da modificação parcial da superfície externa de NaY com grupos alquilsilanos. As partículas adicionadas a uma mistura contendo água e 1,2-epoxioctano foram facilmente localizadas na interface das fases líquido-líquido, e catalisaram eficientemente a hidratação do epóxido, mesmo sem agitação. Com o objetivo de investigar o efeito da localização dos sítios ativos, foram preparados HZSM-5 alquilsililado e NaY funcionalizado com ácido sulfônico, em que os sítios ativos estão localizados predominantemente na superfície interna dos zeólitos. Neste caso, foi necessária agitação mecânica para aumentar a velocidade de reação. Sugere-se que a alquisilação da superfície externa do zeólito, quando o sítio ativo se encontra principalmente dentro do poro, não pode modificar o modo de ação do catalisador; ainda é necessário agitar a mistura reacional para promover a transferência de massas de substratos e reagentes.

The catalytic potential of phase-boundary catalyst for acid-catalyzed reactions has been demonstrated by NaY zeolite loaded with alkylsilane-covered niobic acid in the liquid phase hydration of 1,2-epoxioctane with water. The catalyst was prepared by impregnation of niobic acid on the external surface of NaY and followed by a partial modification of the external surface of NaY with alkylsilyl groups. When the particles were added to a mixture of water and 1,2-epoxioctane, they were feasibly located just at the liquid-liquid phase boundary and efficiently catalyzed hydration of the epoxide even without stirring. In order to investigate the effect of the location of the active sites, alkylsililated HZSM-5 and sulfonic acid functionalized NaY in which the active sites are located dominantly on the internal surface of zeolites were prepared. In that case, mechanical stirring was needed to increase the reaction rate. It was suggested that alkylsilylation on the external surface of zeolite, when the active site is mainly inside the pore, could not change the mode of the catalytic action; it is still necessary to stir the reaction mixture to drive the mass transfer of substrates and reagents.

Keywords: phase-boundary catalysis, acid-catalyzed reactions

Introduction

The fast-growing insight into green chemistry has led the research to focus in the area of environmentally benign catalysts.1,2 Along this line, we recently reported a novel concept of the “phase-boundary catalysis (PBC)”3-6 in order to utilize an immiscible liquid-liquid system using a solid catalyst. Several authors have reported such triphase system in which the homogeneous modification of a particulate catalyst loaded with metal ions or their complexes as active sites induced or accelerated the catalytic reaction of organic substrate with aqueous solution.7,8 In such triphase systems, however, vigorous stirring, leading to sufficient mass transfer, is required to drive the reaction. Another important concept in order to utilize an immiscible liquid-liquid system is “phase-transfer catalysis”. The term, “phase-transfer catalysis”, was originally introduced by Starks to characterize a process in which: “reaction is brought about the use one reactant across the interphase into the other phase so that reaction can proceed”.9 In this...
system, the agitation is also needed to mechanically shuttle the catalyst from one liquid phase to the other. Our strategy is different from those previously reported because we aim at placing the bifunctional particles, containing both hydrophilic and hydrophobic regions, as well as the active sites at the phase boundary in order to catalyze the reaction without any transports the substrate across the interphase and without the formation of an emulsion containing a catalyst by vigorous stirring. Proposed model of phase-boundary catalyst is shown in Figure 1. This system offers advantages in terms of ease of separation, the possibility of continuous supply of immiscible substrates and working effectively without co-solvent. This phenomenon was observed when the external surface of zeolites is covered partially with hydrophobic alkylsilyl groups.

Previously, we reported the PBC for the oxidation reactions using aqueous H₂O₂. In this paper, the study of PBC is now extended for acid catalysis in which the hydration of 1,2-epoxyoctane using zeolite loaded niobium oxide covered by alkylsilane is chosen as model catalytic system.

**Experimental**

**Catalysts preparation**

**Alkylsilylated HZSM-5.** HZSM-5 (JRC-Z5-90H(1)) powder was supplied by the Catalysis Society of Japan and used as received. The SiO₂/Al₂O₃ ratio and surface area of HZSM-5 were 90 and 300 m² g⁻¹ respectively. Unmodified HZSM-5 is called w-HZSM-5. Partly modified ZSM-5 on which the external surface was partly covered with alkylsilane was prepared by attachment of n-octadecyltrichlorosilane (ODS). This preparation method is same as given in our recent papers. In a typical experiment, in order to modify HZSM-5 with alkylsilane, the w-HZSM-5 powder containing water (0.5 – 0.9 g per 1.0 g of w-HZSM-5) was immersed in 5 mL toluene containing 500 μmol of n-octadecyltrichlorosilane (ODS, ShinEtsu) and the suspension was shaken for ca. 5 minutes at room temperature. Then, the solid was collected by centrifugation and dried at 383 K for 5 h. The partly modified sample was labeled w/o-HZSM-5. Fully modified HZSM-5 (o-HZSM-5) was prepared without the addition of water.

**Passivation of the external surface of HZSM-5.** In the first step, n-octadecyltrichlorosilane (ODS) is attached by full coverage, with a similar procedure for making o-HZSM-5. In the second step, the powders obtained were calcined at 500 °C for 5 h in order to make the external surface of HZSM-5 coated by silica layer. The solids obtained were further modified with ODS at a similar procedure in the preparation of w/o-HZSM-5 and o-HZSM-5. They were labeled as w-Si-HZSM-5, w/o-Si-HZSM-5 and o-Si-HZSM-5.

**Sulfonic acid functionalized NaY.** NaY zeolite (JRC-Z-Y5.5) was supplied by the Catalysis Society of Japan and used as received. The SiO₂/Al₂O₃ ratio and surface area of NaY zeolite were 5.5 and 700 m² g⁻¹ respectively. Sulfonic acid covered NaY zeolite was prepared according to the literature. In typical experiment, before modification, NaY zeolite is calcined at 400 °C for 2 h in order to remove adsorbed water. Calcined NaY zeolite (3 g) is added to a solution of 3-mercaptopropyl trimethoxysilane (MPTS, Wako) (0.294 g) dissolved in toluene (20 mL) as the organosulfonic acid precursor. Toluene was dried over zeolite 4A before use. The molar amount of sulfonic acid (SO₃H) was 500 μmol g⁻¹ zeolite. After 4 h refluxing, the powder is collected and washed with CH₂Cl₂/Et₂OH (1:1) (50 mL) and air-dried.

Materials with immobilized mercaptopropyl groups were oxidized with H₂O₂ in methanol-water mixture. Typically, 6 mL 30% H₂O₂ dissolved in 18 mL methanol. After 24 h, the suspension was filtered, and washed with H₂O and EtOH. The wet material was resuspended (3 wt%) in 0.1 mol L⁻¹ H₂SO₄ for 2 h. Finally, the materials were extensively rinsed with H₂O and dried at 333 K under vacuum. These acid materials are denoted with SO₃H-NaY.

Partly modified SO₃H-NaY in which the external surface was partly covered with alkylsilane from ODS was prepared with the same procedure for making w/o-HZSM-5 and labeled as w/o-SO₃H-NaY. Unmodified and fully modified SO₃H-NaY were labeled as w-SO₃H-NaY and o-SO₃H-NaY respectively.

**Niobic acid functionalized NaY.** NaY zeolite covered niobic acid (Nb-NaY) was prepared by impregnation of...
niobium pentaethoxide ([Nb(OEt)₅]) from its ethanol solution at room temperature. The molar amount of Nb was 500 μmol g⁻¹ zeolite. Unmodified Nb-NaY is called w-Nb-NaY. Modified Nb-NaY on which the external surface was partly covered with alkylsilane was prepared by attachment of n-octadecyltrichlorosilane (ODS). This preparation method is same as given in preparation of alkylsilylated HZSM-5. The partly modified sample was labeled w/o-Nb-NaY and o-Nb-NaY for fully modified.

**Reaction conditions**

Hydration of cyclohexene was carried out using the above catalysts. Cyclohexene (2 mL), water (2 mL) and catalyst powder (50 mg) were placed in a glass tube, and the reaction was performed with or without stirring at 70 °C for 20 h after removal of oxygen by argon bubbling. Hydration of 1,2-epoxyoctane with water was carried out at 70 °C for 20 h. In detail, 1,2-epoxyoctane (1 mL), water (1 mL) and catalyst powder (25 mg) were placed in a glass tube, and the reaction was performed with or without stirring. The reaction products of the above reactions were analyzed by gas chromatography (Shimadzu GC-14B with FID and DB-1 column) and GC/MS.

**Results and Discussion**

**Effect of stirring on the location of active sites**

Figure 2 shows the yield of cyclohexanol in the hydration of cyclohexene with water over w-HZSM-5, w/o-HZSM-5 and o-HZSM-5. The first effect observed from this figure is that the stirring is required to increase the reaction rate. Our early results in the epoxidation reactions³⁻⁵ indicate no mass transfer limitation observed when the active sites were located on the external surface of zeolite and the catalyst particles were placed at the liquid-liquid boundary, therefore we conclude that the activity of catalyst does not depend on the stirring rate. On the other hand, this phenomenon could not be applied for hydration of cyclohexene by w/o-HZSM-5 even though the catalyst was successfully placed at the liquid-liquid boundary. Furthermore, diffusion resistance becomes dominant factor in this triphasic mode reaction. This can be explained on the basis of the location of active sites of HZSM-5, which are located predominantly inside the pore, and not on the external surface. Based on this consideration, the role of the external active sites in the reaction could be examined by passivating the external surface of zeolite with silica layer coating, where this layer has been considered not to be active for hydration of cyclohexene. Figure 3 shows the trend of the catalytic activity of w-Si-HZSM-5, w/o-Si-HZSM-5 and o-Si-HZSM-5 (passivated HZSM-5s). Although the results show no significant effect of this approach for the trend of catalysts’ activities, under static conditions, the yield of passivated HZSM-5 exhibit a yield 5% lower when compared to unpassivated HZSM-5. This suggests that the active sites located on the external surface give a contribution for increasing the catalysts’ activity under static conditions, although their contribution to the overall reaction is small.

**Nature of active sites**

Catalytic activities as depicted in Figures 2 and 3 indicate w-HZSM-5 is the most active catalyst for hydration of cyclohexene. In our previous reports,⁶⁻⁸ it was explained that the highest catalytic activity has a correlation to the location of catalysts’ particles, in which the solid catalyst was placed at the liquid-liquid phase boundary. Obviously, this argument does not hold for the w-HZSM-5 since the enhancement of the rate cannot be solely attributed to the distribution of catalysts in liquid-

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**Figure 2**. The yield of cyclohexanol in organic phase on the hydration of cyclohexene using various modified HZSM-5 under static and stirring conditions. All reactions were carried out at 70 °C in argon atmosphere for 20 h: 50 mg catalyst; 2 mL cyclohexene and 2 mL water.

**Figure 3**. The yield of cyclohexanol in organic phase on the hydration of cyclohexene using various modified HZSM-5 under static and stirring conditions. Reaction conditions are the same as given for Figure 2.
liquid system and location of their active sites. The effect of HZSM-5 intrinsic properties such as the existence of active sites in the framework and its MFI structure play an important role in the catalytic activity. These properties certainly give a synergy effect for the catalytic activities with hydrocarbons. To exclude the possibility of these characteristics, sulfonic acid (SO$_3$H) anchored on the surface of NaY zeolite was used as a catalyst model. Since the molecular size of MPTS (ca. 0.55 nm) is smaller than pore size of NaY zeolite (ca. 0.70 nm), it is expected that the deposition of SO$_3$H occur on the internal surface of zeolite. This catalyst was used for acid catalysis in the system containing cyclohexene and water.

As shown in Figure 4, all the systems containing modified sulfonic acid functionalized zeolites (w-SO$_3$H-NaY, w/o-SO$_3$H-NaY and o-SO$_3$H-NaY) produce 2-methyl-2-cyclopenten-1-one as a major product as analyzed by GC/MS. A similar compound was also observed when 0.1 mol L$^{-1}$ H$_2$SO$_4$ was used instead of those catalysts in the same experimental conditions (Figure 4). With a w/o-SO$_3$H-NaY, under stirring conditions, the activity (i.e., the peak area of the 2-methyl-2-cyclopenten-1-one per amount of SO$_3$H) more than triples compared to the mixture containing H$_2$SO$_4$. This indicates that the w/o-SO$_3$H-NaY is particularly capable of catalyzing the reaction at the liquid-liquid phase-boundary. However, the mechanism of this reaction was not fully understood. It could be that the carbenium ion and ring contraction occur within the mechanisms. In order to investigate heterogeneity, the catalysts were suspended in water and stirred for 2 h at 70 °C. After filtration, the water, without the catalyst, was vigorously stirred for 20 h with addition of cyclohexene. This system exhibits no activity suggesting the reaction occurs on the catalyst particles, but not due to the leached SO$_3$H species. It should be noted that the mass transfer limitations may be a place constraint on SO$_3$H-NaY catalysis because of the location of SO$_3$H is mainly inside the pore of NaY. It is clearly shown in Figure 4 that these mass transfers are further enhanced by the mechanical agitation. For comparison, modified SO$_3$H-NaY catalysts were also used to catalyze the hydration of 1,2-epoxyoctane to 1,2-octanediol, and the results are shown in Figure 5. It showed that the activity of modified SO$_3$H-NaY was also always higher when mechanical agitation was applied for the system. Similar to the hydration of cyclohexene (Figure 3), the results in Figure 5 showed that w/o-SO$_3$H-NaY also gave a higher activity compared to w-SO$_3$H-NaY and o-SO$_3$H-NaY. One possible explanation is that the bimodal amphiphilicity character of w/o-SO$_3$H-NaY gives a large contribution to the catalytic activity. This argument was supported by the distribution of catalysts during the reaction under static conditions; w/o-SO$_3$H-NaY was located at the liquid-liquid phase boundary, whereas w-SO$_3$H-NaY and o-SO$_3$H-NaY were dispersed in aqueous and organic phases respectively.

According to the catalytic activity of the alkylsilylated HZSM-5 and sulfonic acid functionalized NaY as catalyst models of acid-catalyzed reactions, the specific role of location and nature of the active sites was examined. The two effects may indeed account for the observed catalytic activity of the catalysts in the liquid-liquid system under static and stirring conditions. Thus, our task here is to confirm the effect of active site which is located at the external surface of zeolite. Based on this purpose, niobic acid functionalized NaY has been chosen as another catalyst model. Although there is no experimental evidence at present, Nb active sites should be attached to the external surface of NaY since the estimated molecular size of Nb(OC$_2$H$_5$)$_5$ is larger than the size of pore-entrance of NaY (ca. 0.70 nm).
The dispersion behavior of w/o-Nb-NaY, prepared with different amount of added water to form Nb-NaY aggregates before attachment of alkyl groups, and o-Nb-NaY are shown in Figure 6. From their dispersibility, more water is added to Nb-NaY, resulting more hydrophilic w/o-Nb-NaY particles. It was found that the addition of ca. 60 – 70 wt% water per g Nb-NaY gave the highest yield of 1,2-octanediol. Addition of more than 90 wt% water per g Nb-NaY can make the powder totally wetted by water in the form of ‘wet cake’. After attachment of alkylsilyl groups, the resulting alkylsilylated particles seemed heterogeneous; some particles were located at the phase-boundary while others were dispersed in water.

It should be noted that alkylsilyl groups should be attached to the external surface of NaY zeolite since the estimated molecular size of alkylsilane (ca. 0.50 nm x 2.60 nm), the source of alkylsilyl, larger than the size of pore-entrance of NaY zeolite (ca. 0.70 nm). The distribution of alkylsilyl groups on the external surface of w/o-NaY has been clarified by using fluorescence microscopy; each w/o-NaY particle has both hydrophobic and hydrophilic surfaces; i.e., one side is covered with alkylsilyl groups and the other is kept covered with hydroxyl groups (silanols). Details for this fluorescence microscopic study was reported recently. Because of this surface characteristic, the modified particles are spontaneously located at the interphase in a W/O mixture with the hydrophilic side facing the organic phase and the hydrophobic side facing the aqueous phase.

As demonstrated in the previous paper, in the water adsorption experiment, it was observed that the adsorption capacity of OTS-modified NaY particles at ambient temperature (8 mmol g⁻¹ for both w/o-NaY and o-NaY) was not so different from that of the parent NaY zeolite (11 mmol g⁻¹), indicating that the structure and hydrophilic features of internal pores of these NaY particles were retained and that the hydrophobic alkyl chains did not block the entrance of zeolite pores.

When the above catalysts were used in reaction system containing 1,2-epoxyoctane and water, it was observed that, after four hours reaction, under stirring condition, the emulsion was formed in the system containing w/o-Nb-NaY, whereas o-Nb-NaY was still located at organic phase due to its hydrophobicity in nature (Figure 7). Instead distinctly, the w-Nb-NaY was well dispersed in aqueous phase. This suggests that w/o-Nb-NaY possess amphiphilic character to stabilize the immiscible mixture of organic and aqueous phases.

As shown in Figure 7, all the system containing modified niobic acid functionalized zeolite (w-Nb-NaY, w/o-Nb-NaY and o-Nb-NaY) produced 1,2-octanediol as a major product. The w/o-Nb-NaY gave highest yield of diol in comparison to the w-Nb-NaY and o-Nb-NaY. It is notable that the activity of w/o-Nb-NaY was independent of the stirring rate; i.e., this catalyst does not require the formation of the emulsion by stirring at ca. 1000 rpm. One needs to consider that the hydrophilic and hydrophobic parts of the w/o-Nb-NaY play an important role for continuous supply of the organic and aqueous substrates to the active sites, and increase the activity.

![Figure 6](image1.png)

**Figure 6.** The distribution of various modified Nb-NaY in the mixture of 1,2-epoxyoctane and water: (a) o-Nb-NaY, (b) w/o-Nb-NaY with the amount of added water to form Nb-NaY aggregates before attachment of ODS is 88% wt water per g Nb-NaY and (c) 50% wt water per g Nb-NaY.

![Figure 7](image2.png)

**Figure 7.** The yield of 1,2-octanediol in organic and aqueous phases on the hydration of 1,2-epoxyoctane using various modified Nb-NaY, under static and stirring conditions. Reaction conditions are the same as given for Figure 5. The photograph shows the distribution of solid catalyst after 4 h reaction.
The hydration rate of 1,2-epoxyoctane under static condition is shown in Figure 8. It was observed that the reaction rate was considerably slow. Due to no significant quantitative yield was observed in the first 30 minutes, the reaction was extended to 20 h. It confirms that significant difference in the rate of the reaction between w-Nb-NaY, w/o-Nb-NaY and o-Nb-NaY is observed.

It has been reported in the previous paper that NaY, having a microporous structure with a relatively large surface area, was preferable as a support in this system compared with nonporous silica with a smaller surface area.4. One considers that Nb active sites on the NaY surface can be in contact with both organic substrate and water. During the reaction at the Nb sites, due to the decrease in the concentration of substrate and water at the interphase, the concentration gradient of these reagents may appear in both organic and aqueous phases; this gradient may generate a driving force to supply these reagents from respective bulk solutions, thereby enabling the reaction to proceed efficiently without any enforced manipulation, such as stirring, in order to drive liquid–liquid mass transfer. In order to achieve this, the catalyst must satisfy the following requirements: (i) existence of active Nb sites at the liquid–liquid phase boundary, and (ii) continuous supply of both substrates through the hydrophobic and hydrophilic parts of the catalyst particles. Therefore, if the catalyst particles consist of nonporous materials, the number of Nb active sites are limited and efficient PBC cannot be expected (see Figure 1). The use of a microporous material as a support must increase the effective interphase area of the catalyst (i.e., increase the number of active sites), resulting in higher activity.

Attachment of alkylsilane on the niobic acid sites is another possibility cause lowering activity of o-Nb-NaY compared to w/o-Nb-NaY. In order to exclude this argument, the Temperature Programme Desorption (TPD) of ammonia experiments were performed on w-Nb-NaY, w/o-Nb-NaY and o-Nb-NaY. It was observed that no significant difference in the amount of acid sites from calculation of desorbed ammonia amount within the samples.14 This suggests that the acid sites on the modified samples are not attached by ODS.

Conclusions

In this study, the phase-boundary catalysis concept was applied for acid-catalyzed hydration of 1,2-epoxyoctane with water by NaY zeolite loaded with alkylsilane-covered niobic acid. This system did not require stirring to make an emulsion to drive the hydration. The nature of acid sites and their location, whether in the pore or on the external surface of zeolite, are important factors for the catalytic activity of phase-boundary catalysts for acid catalysis.

References


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Simultaneous adsorption of a mixture of paraquat and dye by NaY zeolite covered with alkylsilane

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Abstract

The surfaces of NaY zeolite particles were modified by the alkylsilylation of n-octadecyltrichlorosilane (OTS). Two kinds of modified NaY zeolites were prepared; one with its external surface partially and the other fully covered with alkylsilyl groups. Since the size of OTS is bigger than the pore diameter of NaY, it is attached on the external surface, leaving the internal pore accessible to adsorbate molecules. As a result of alkylsilylation, the adsorption properties of these sorbents were improved. The adsorption properties of these materials were tested by their reaction in a mixture of paraquat and blue dye. The results demonstrate that the alkylsilylated NaY materials are capable of simultaneous adsorption of paraquat and blue dye. Paraquat was selectively adsorbed into the internal pore of the zeolite whereas the dye on the externally attached alkylsilyl groups of the sorbent; displaying the unique bimodal amphiphilic character of the alkylsilylated NaY zeolites.

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Keywords: Paraquat; Blue dye; Alkylsilylation; NaY zeolite.

1. Introduction

The removal of hazardous organic materials from wastewater is one of the most important environmental issues to be solved today [1]. In real life situation, these materials are usually present as a mixture of hydrophilic and hydrophobic organic compounds. The objective of this study is to design an adsorbent for adsorption of organic materials, specifically the removal of both hydrophilic and hydrophobic organic compounds from water. For this purpose, a mixture of hydrophilic herbicide and hydrophobic dye are used as the model adsorbates. The application of herbicide and dye in agriculture and industries have been detrimental to the environment. Therefore, it is necessary to remove these hazardous materials from water as much as possible [2–4]. The commonly used herbicide and dye are paraquat and blue dye, respectively. Paraquat (1,1′-dimethyl-4,4-bipyridinium dichloride, PQ), a quaternary nitrogen herbicide, is a highly toxic compound and many cases of acute poisoning and death have been reported over the past few decades [1]. In order to prevent accidental deaths due to confusion with cola, black coffee or other beverages, a blue dye, as a colouring agent, was added to commercial PQ [5]. The use of dyes may also pose some level of human risk. Unfortunately, the ingredients in blue dye are considered proprietary. In general, the dye used is hydrophobic and its chemical structure is bigger than that of PQ [5]. In order to rationalize the adsorption of blue dye, the reactive dye Cibacron Blue 3GA (CB3GA); having the well-known structure shown in Fig. 1 was used.

Alkylsilylation of mesoporous materials has been reported in an attempt to prepare materials for extraction of metal ions [6,7]. The surface properties of zeolites have also been modified by alkylsilylation [8–10]. Recently a new approach in modifying the surface of zeolite by the alkylsilylation of n-octadecyltrichlorosilane (OTS) onto the NaY zeolite particles, resulting in hydrophobic zeolites; having
Fig. 1. Chemical structure of Cibacron Blue 3GA.

their surface partially and fully covered with alkylsilyl groups was reported [11,12]. Proposed models of the modified NaY zeolites are depicted in Fig. 2. In the present study, it is demonstrated that the modified NaY zeolite particles can adsorb both PQ and blue dye simultaneously. PQ is preferentially adsorbed on the hydrophilic internal pore whereas blue dye, being hydrophobic is adsorbed on the external surface area of the modified zeolite particle. The effect of partial alkylsilylation on the surface of NaY zeolite on the adsorption of PQ and blue dye is also discussed.

2. Experimental

2.1. Surface modifications

NaY zeolite (CBV100) supplied by Zeolyst International with a surface area of 900 m$^2$ g$^{-1}$ was used as received. Modified NaY in which the external surface was partially covered with alkylsilane was prepared by attachment of $n$-octadecyltrichlorosilane (OTS), prepared according to the method reported previously [11,12]. Typically, the NaY powder containing water (0.25, 0.50, 0.75 and 1.0 g per gram of NaY) was immersed in 5 ml toluene containing 500 μmol of OTS (Aldrich) and the suspension was shaken for 5 min at room temperature. Then, the solid was collected by centrifugation and dried at 110$^{\circ}$C for 5 h. Addition of a small amount of water to the hydrophilic NaY surface led to aggregation due to the capillary force of water between particles. Under these conditions, it is expected that only the outer surface of aggregates, which is in contact with the organic phase can be modified with OTS. The partially modified sample was labeled w/o-NaY. Fully modified NaY labeled as o-NaY was prepared without the addition of water.

In order to establish their surface structures, each w/o-NaY and o-NaY sample (0.06 g) was added into an immiscible mixture of $n$-hexane (2 ml) and water (2 ml). Then, the mixture was stirred vigorously at 1000 rpm for 2 h and kept under static condition for 12 h. The capability of the particles to stabilize the liquid–liquid system to form an emulsion was attributed to their hydrophobic-hydrophilic character and hence their surface structure [13,14].

Photographs of emulsion formed in the presence of modified NaY zeolites were taken under an optical microscope. In order to specify whether the type of emulsion was oil-in-water (o/w) or water-in-oil (w/o), hydrophilic methylene blue was used as the indicator.

Study on the adsorption kinetic of adsorbed water was carried out in order to determine its role in the determination of the adsorption capacity and alkylsilyl coverage of the modified NaY samples. About 1 g of modified NaY sample was dehydrated under vacuum at 100$^{\circ}$C overnight. After dehydration, the sample was exposed to water vapour at room temperature, followed by the determination of the percentage of adsorbed water as a function of time.

2.2. Adsorption of dyes and paraquat

The dye used was Cibacron Blue 3GA (CB3GA) from Sigma. Adsorption was carried out by stirring 20 ml of 500 ppm CB3GA solutions in the presence of 0.4 g of modified NaY samples at room temperature. The adsorption kinetics experiments were carried out in a 50 ml Pyrex glass bottle. Modified NaY adsorbents were used after degassing at 100$^{\circ}$C overnight in the vacuum oven. The CB3GA solutions were contacted for 2 h and analyzed spectrophotometrically at $\lambda_{\text{max}}$ of 601 nm.

A commercial PQ (18.3%) by Bayer in the presence of blue dye as the coloring agent was used in the adsorption experiments. The intensity of the blue colour of the dye is used as a measure of concentration. Adsorption was carried out by stirring 25 ml of 300 ppm PQ solutions at room temperature. The PQ solutions were contacted for 5, 10, 15, 30 and 60 min with 0.4 g modified NaY zeolite, after degassing at 100$^{\circ}$C overnight in the vacuum oven. The PQ and blue
dye concentration analysis of filtrate was carried out at $\lambda_{\text{max}}$ of 256 and 634 nm, respectively. Adsorption kinetic experiments were immediately conducted with 1.0 cm light path quartz cells using Perkin-Elmer Lambda 900.

3. Results and discussion

3.1. Physical properties

In this part, the physical properties of alkylsilane-modified NaY zeolites are discussed in order to clarify the effects of alkysilylation to their surface properties. The follow-on part, the surface properties of the adsorbents are correlated to the character of dye and paraquat which are adsorbed on them.

The dispersion behaviour of partially silylated NaY sample (w/o-NaY) and totally silylated NaY sample (o-NaY) are shown in Fig. 3. The dispersibility indicates that as more water is added to NaY, the more hydrophilic is the resulting w/o-NaY particles. It was found that the addition of more than 90 wt.% water per gram NaY could totally wet the powder to form the ‘wet cake’. After attachment of alkylsilyl groups, the resulting particles seemed heterogeneous; some particles were located at the phase-boundary while others were dispersed in water (see Fig. 3(b)). The addition of ca. 50 wt.% water per gram NaY gave the highest stability; locating the w/o-NaY particles at the phase-boundary as observed in Fig. 3(c). Results in Fig. 3 suggest that there is a correlation between alkylsilyl coverage on the surface of NaY with the distribution of modified NaY in the hexane–water mixture. This argument is clarified with the water adsorption experiments.

As shown in Fig. 4, it was clearly observed that the amount of adsorbed water on o-NaY was significantly lower than those of w/o-NaY and NaY. Apparently, the amount of water added before alkylsilylation led to changes in alkylsilyl coverage on the surface of modified NaY. The higher the amount of water added, the lower was the alkylsilyl coverage. It is obvious that alkylsilyl groups should be attached to the external surface of NaY zeolite since the estimated molecular size of alkylsilane (ca. 0.50 nm × 2.60 nm), the source of alkylsilyl, is larger than the size of the entrance pore of NaY zeolite.

![Fig. 3](image_url)

Fig. 3. The photographs show the distribution of (a) NaY, (b)–(d) w/o-NaY and (e) o-NaY solid particles when added to hexane–water mixture. The w/o-NaY was prepared with the amount of added water to form NaY aggregates before attachment of OTS was (b) 1.00 g, (c) 0.50 g and (d) 0.25 g water per gram NaY.

![Fig. 4](image_url)

Fig. 4. Percentage of adsorbed water on the surface of (a) NaY, (b)–(d) w/o-NaY and (e) o-NaY. The modified NaY used are the same as in Fig. 3.
Fig. 5. The photographs showing the distribution of NaY, w/o-NaY and o-NaY solid particles (a) when added to hexane-water mixture, (b) after stirring for 2 h and (b) after keeping under static conditions for 12 h. The w/o-NaY used is the same solid particles used in Fig. 3(c).

Fig. 5 shows the distributions of the NaY, w/o-NaY and o-NaY samples in a mixture of n-hexane and water, after stirring for 2 h and keeping under static conditions for 12 h. It confirms that sample w/o-NaY (solid particles in Fig. 3(c)) is located at the liquid–liquid boundary mixture of n-hexane and water, whereas NaY and o-NaY are dispersed in aqueous water and organic n-hexane phase respectively. One expects that if the solid particles were able to be located at the phase-boundary, these particles may act as an effective emulsifying agent. To confirm this consideration, the mixture was then stirred. It was observed that emulsion was formed in the system containing w/o-NaY and o-NaY (Fig. 5(b)). In the emulsion form, the specific interfacial interactions between the particles surface and the two immiscible liquid phases increased the surface contact (wettability) of the particles with the organic and aqueous phases. For maximum efficiency, the particles should be wetted preferentially by the two liquid phases. If the solid particles were too strongly wetted by either of the two liquid phases, the required stabilizing action would not result [15]. To confirm this, the stability of the emulsion in the presence of the solid particles was examined. Interestingly, the emulsion was stabilized by w/o-NaY for up to 12 h, whereas stability of emulsion of the system containing o-NaY was only 1 h. As shown in Fig. 5, it is clearly demonstrated that an emulsion has been formed, resulting in an abrupt visual homogenization. In contrast, no emulsion was formed in the system containing NaY, which suggests that w/o-NaY possesses a good bimodal amphiphilic character that stabilizes the immiscible mixture of organic and aqueous phases to form a more stable emulsion.

Fig. 6 shows the optical microscope photographs of the type of emulsion formed; the o-NaY and w/o-NaY act as emulsifiers to stabilize the n-hexane and water mixture forming the water-in-oil type emulsion. In order to correlate the amphiphilic character with the surface structure, a fluorescence microscopic study was carried out [16]. It has been established that each w/o–NaY particle has both hydrophobic and hydrophilic surfaces. Therefore, the results described above are experimental evidence to the proposed models shown in Fig. 1.

### 3.2. Adsorption of dye and paraquat

Fig. 7 shows the adsorption of CB3GA by various modified NaY. The amount of adsorbed CB3GA decreased with decreasing hydrophilicity of adsorbent. NaY did not adsorb CB3GA. This result confirms that CB3GA is adsorbed by the alkylsilyl groups. The trend in adsorption implies that there is a correlation between the surface coverage of alkylsilyl groups and the adsorption capacity of the modified NaY as supported by the adsorption experiments of water shown in Fig. 4. The higher is the alkylsilyl coverage, the lower is the adsorption capacity of water and hence the higher is the adsorption of CB3GA. If the w/o-NaY has a bimodal amphiphilic surface structure; where one side of the external surface is hydrophilic and the other is hydrophobic, then a mixture of hydrophilic and hydrophobic compounds could be adsorbed simultaneously by this system. To confirm this expectation, a mixture containing hydrophilic PQ and hydrophobic blue dye was used as adsorbates.

As shown in Fig. 8, all systems containing zeolites: NaY, w/o-NaY and o-NaY can adsorb PQ. The degree of the rate of adsorption of PQ in decreasing order is as follows: NaY > w/o-NaY > o-NaY. In comparison, the degree of the rate of adsorption of blue dye in decreasing order is as follows: o-NaY > w/o-NaY > NaY, although at the beginning (upto 5 min), the adsorption rate of w/o-NaY is faster than that of o-NaY (Fig. 9). It is also shown that NaY does not adsorb either blue dye or CB3GA at all.

Results in Figs. 8 and 9 show that despite blue dye not being adsorbed at all, the adsorption rate of PQ by NaY is

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**Fig. 5** The photographs showing the distribution of NaY, w/o-NaY and o-NaY solid particles (a) when added to hexane-water mixture, (b) after stirring for 2 h and (b) after keeping under static conditions for 12 h. The w/o-NaY used is the same solid particles used in Fig. 3(c).
relatively fast. In contrast, the adsorption rates of PQ and blue dye by o-NaY are slow and fast, respectively. This evidently suggests that although the C18 chains on the o-NaY has high hydrophobicity, the network still has channels which are available to PQ even though at a considerably slow rate. It also confirms that C18 chains on the w/o-NaY and o-NaY play a role in the adsorption of the dye molecules. The w/o-NaY simultaneously adsorbs PQ and blue dye, although at a considerably slower rate than that of NaY and o-NaY.

From the above results, the adsorption behaviour of modified NaY particles could be rationalized by correlating it with their amphiphilic character and hence their surface structure. It is possible that the hydrophilic and hydrophobic regions of w/o-NaY, as shown in Fig. 2(a), play an important role in the eventual adsorption of the PQ and blue dye. PQ is adsorbed easily by entering the pore through the hydrophilic part, whereas the blue dye molecule is adsorbed on the alkylsilyl...
Fig. 9. Adsorption of blue dye on NaY, w/o-NaY and o-NaY. All experiments were done similar to that of the adsorption conditions shown in Fig. 8. In case of o-NaY, the adsorption of PQ in the pore is retarded by the hydrophobic alkylsilyl groups which are located on the fully covered external surface (see Fig. 2(b)). However, at present, we only demonstrate the application of this adsorbent system in the adsorption of commercial PQ containing blue dye as a model. The adsorption of the other chemical systems is currently being studied in our laboratory.

4. Conclusions

The results described above indicate that NaY zeolite loaded with alkylsilane is particularly capable of simultaneous adsorption of paraquat and blue dye. The adsorption rates of the paraquat and blue dye were affected by the surface coverage of alkylsilyl groups on NaY. Paraquat was adsorbed on the pore, relatively easier, with the presence of hydrophilic part on the external surface of partially alkylsilylated NaY zeolite. On the other hand, the dye molecule was adsorbed on the alkylsilyl groups. If the external surface of the NaY zeolite particles was completely covered with alkylsilyl groups, the adsorption of paraquat was retarded because it must overcome the barrier of the hydrophobic alkylsilyl groups. In conclusion, a novel integrated chemical system consisting of a modified alkylsilane-modified porous particles capable of simultaneous adsorption of a mixture of hydrophilic and hydrophobic organic compounds has been demonstrated.

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Hydrophobic fluorinated TiO₂–ZrO₂ as catalyst in epoxidation of 1-octene with aqueous hydrogen peroxide

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Abstract

A new heterogeneous oxidation catalyst was prepared by impregnation of TiO₂ from titanium(IV)tetra-2-propoxide on the surface of ZrO₂. The surfaces of TiO₂–ZrO₂ particles were then modified by the fluorination of ammonium hexafluorosilicate and followed by alkylsilylation of n-octadecyltrichlorosilane (OTS). The resulting catalysts were characterized by X-ray diffraction (XRD), nitrogen adsorption isotherm, UV–Vis Diffuse Reflectance (UV–Vis DR), and Energy Dispersive X-Ray Analysis (EDAX) techniques. The catalytic potential of catalysts for oxidation reactions has been verified in the liquid phase epoxidation of 1-octene to 1,2-epoxyoctane with aqueous hydrogen peroxide. It is demonstrated that the fluorination and alkylsilylation enhance the catalytic activity of TiO₂–ZrO₂. A high catalytic activity of the modified TiO₂–ZrO₂ was related to the modification of the local environment of titanium active site and increasing the hydrophobicity of catalyst particles by fluorination and alkylsilylation.

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Keywords: Hydrophobic fluorinated TiO₂–ZrO₂; Epoxidation; Fluorination; Alkylsilylation

1. Introduction

It is generally accepted that heterogeneous catalysis has many advantages compared to the homogeneous system. However, there is the limitation of the application for this system, especially for zeolite. For example, serious drawback has been found for TS-1 due to its restriction to substrate molecules with kinetic diameter <5.5 Å. In TS-1, the active sites for the material are located in the internal framework [1–3] and this limits the application to substrates with relatively small molecular sizes [4]. Large molecules with ring structures are not accessible, reducing its catalytic capabilities. It was explained that the high catalytic activity of TS-1 has a correlation to its intrinsic properties such as the existence of Ti in the framework and its MFI structure [1–3]. These properties certainly give a synergy effect on the catalytic activities of hydrocarbons. Due to the importance of Ti active sites, there is a need to design a system where they can be located at the surface which enables it to freely interact with every substrate. Based on this problem, in this paper, a new catalytic system, hydrophobic fluorinated TiO₂–ZrO₂ is proposed as an oxidation catalyst. The catalyst particles were prepared by deposition of titanium species from titanium(IV)tetra-2-propoxide onto non-porous ZrO₂ and followed by fluorination of ammonium hexafluorosilicate and attachment of octadecylsilyle groups from n-octadecyltrichlorosilane (OTS). Here, zirconia is used as the support because this material is resistant to fluorination. By using this new system, it is expected that any kind of substrate can freely interact with catalytic active site which is located on the surface of the catalyst. To examine this catalytic system, the epoxidation of 1-octene by using aqueous H₂O₂ was chosen as a model reaction.

2. Experimental

2.1. Preparation of catalysts

In a typical experiment, in order to synthesize Ti–ZrO₂, 1 g of zirconium hydroxide [Zr(OH)₄] (Sigma-Aldrich) is added to a solution of 500 μmol titanium(IV)tetra-2-propoxide [Ti(PrO)₄] (Fluka) dissolved in toluene. Then, the suspension was stirred until the solvent is completely dry and calcined at 500 °C for 2 h.
The fluorination of Ti–ZrO$_2$ series was carried out by immersing Ti–ZrO$_2$ into 1 M ammonium hexafluorosilicate [(NH$_4$)$_2$SiF$_6$] (Aldrich) solution for 10 min and then dried at 383 K overnight to give F–Ti–ZrO$_2$. The F–Ti–ZrO$_2$ was then further modified by alkylsilylation of octadecyltrichlorosilane (OTS, Aldrich) to yield O–F–Ti–ZrO$_2$. Alkylsilylation process was carried out according to the method reported previously [5,6]. In a typical experiment, 1 g of F–Ti–ZrO$_2$ was suspended in 10 ml of toluene solution containing 500 μmol of OTS. Then, the suspension was centrifuged in order to remove excessive unreacted OTS and washed with toluene and ethanol. The precipitate was then dried at 383 K overnight. Hence, the particles obtained were labeled O–F–Ti–ZrO$_2$.

### 2.2. Characterizations

The Ti–ZrO$_2$, F–Ti–ZrO$_2$ and O–F–Ti–ZrO$_2$ were characterized by UV–Vis Diffuse Reflectance (UV–Vis DR), X-ray diffraction (XRD), Energy Dispersive X-Ray Analysis (EDAX) and surface area analyzer. UV–Vis spectra were recorded using Perkin Elmer Lambda 900 spectrometer. XRD patterns were acquired on a Bruker D8 Advance instrument using Cu K$_\alpha$ radiation (λ = 1.5418 Å, 40 kV, 40 mA). Surface area of the catalysts was analyzed using BET surface area analyzer instrument (Thermo Finnegan Qsurf Series). Fluorine element in the catalysts was analyzed with EDAX Philips XL 40 instrument at 20 kV.

Hydrophobicity of catalysts was also analyzed by using water adsorption technique. In a typical experiment, the catalysts were dried in an oven at 383 K for 24 h to remove all the physically adsorbed water. After dehydration, the sample was exposed to water vapor at room temperature, followed by the determination of the percentage of adsorbed water as a function of time.

### 2.3. Catalytic test

To examine the activity of the catalysts, the epoxidation of 1-octene by using aqueous H$_2$O$_2$ was chosen as a model reaction. In the epoxidation reaction, 1-octene (4 ml, Aldrich), 30% aqueous H$_2$O$_2$ (1 ml, Hanns) and catalyst powder (50 mg) were placed in a glass tube, and the reaction was performed with stirring for 24 h at ambient temperature. The resulting product was withdrawn and analyzed periodically with gas chromatograph (GC). Gas chromatograph-mass spectrometer (GC-MS) was also used to verify the resulting product.

### 3. Results and discussion

#### 3.1. Physical properties of catalysts

Fig. 1 shows the XRD patterns of ZrO$_2$, Ti–ZrO$_2$, F–Ti–ZrO$_2$ and O–F–Ti–ZrO$_2$. It is demonstrated that all the modified catalysts possess a similar crystalline structure which is corresponded to monoclinic phase of ZrO$_2$ [7,8]. This result indicates that ZrO$_2$ is highly stable to fluorination and alkylsilylation processes.

Fig. 2 shows UV–Vis DR spectra of Ti–ZrO$_2$, F–Ti–ZrO$_2$ and O–F–Ti–ZrO$_2$. The band in the range of 200–240 nm is attributed to a charge-transfer of the tetrahedral titanium sites between O$_2^−$ and the fluoride ions (F$^−$). The band at around 270 nm is attributed to the presence of F$^−$ ions in the material.
central Ti(IV) atoms, while octahedral Ti was reported to appear at around 260–330 nm [9]. ZrO2 also shows UV absorption bands in the range 200–240 nm as reported previously [10], causing the difficulty to distinguish zirconium species peaks with titanium species peaks in UV–Vis DR spectrum of Ti–ZrO2. However, it shows that, for samples containing fluor (F–Ti–ZrO2 and O–F–Ti–ZrO2), a single high intense band at around 208 nm can be observed. This band is attributable to titanium in the tetrahedral structure. The decrease in intensity in the range of 260–330, which is corresponded to the octahedral titanium, indicates the occurrence of the transformation of some of the octahedral titanium framework to the tetrahedral structure during the fluorination. The surface area of TiO2–ZrO2 (30 m2 g−1), F–Ti–ZrO2 (29 m2 g−1) is almost similar to that of O–F–Ti–ZrO2 (28 m2 g−1) suggesting that there is no effect of fluorination and alkylsilylation on the surface area of the catalysts. The highly stable properties of ZrO2 contribute to unaltered surface area as shown by a similar crystallinity of the modified ZrO2 (see XRD spectra in Fig. 1).

The dispersion behavior of Ti–ZrO2, F–Ti–ZrO2 and O–F–Ti–ZrO2 in immiscible organic–water mixture is shown in Fig. 3. It is clearly observed that after fluorination and alkylsilylation, the resulting modified particles (O–F–Ti–ZrO2 and F–Ti–ZrO2) seemed hydrophobic; some particles were located at the liquid–liquid phase boundary while unmodified Ti–ZrO2 was dispersed in water. However, after a few minutes, the F–Ti–ZrO2 was located in the aqueous phase, whereas O–F–Ti–ZrO2 was still located at liquid–liquid phase boundary due to its hydrophobicity in nature. This observation was supported by water adsorption experiment result. As shown in Fig. 4, it was clearly observed that the amount of adsorbed water on modified Ti–ZrO2 follows the following trend: Ti–ZrO2 > F–Ti–ZrO2 > O–F–Ti–ZrO2. It is suggested that fluor and alkylsilyl groups prevent water from adsorbing on the surface of Ti–ZrO2. Apparently, the fluorination and alkylsilylation led to changes in hydrophobicity of Ti–ZrO2.

The EDAX analysis is a complimentary analysis to check whether the composition of desirable component exists or not in the catalyst since only semi-quantitative result could be obtained using this analysis method. It is calculated that the amounts of zirconium (Zr) and carbon (C) are ca. 55.4 and 19.5 wt.% in O–F–Ti–ZrO2, in which carbon originates from alkylsilyl group attached on the surface of the sample. The amounts of titanium (Ti) and silicon (Si) show only ca. 4.0 and 2.0 wt.% respectively. Fluorine (F) was observed only ca. 1.0 wt.% This result showed that the amount of fluorine in O–F–Ti–ZrO2 is very much lower compared to the amount of ammonium hexafluorosilicate added during the fluorination process (ca. 28%). This suggests that only 1–2 wt.% of fluor is adequate to increase the hydrophobicity of TiO2–ZrO2.

3.2. Catalytic activity

A considerable increase in epoxide yield was observed when the surface of Ti–ZrO2 was fluorinated and alkylsilylated with ammonium hexafluorosilicate and OTS, respectively (see Fig. 5). This phenomenon may be explained in terms of the local environment of Ti active site. As described previously, the difference in the UV–Vis DR spectra of Ti–ZrO2, F–Ti–ZrO2 and O–F–Ti–ZrO2 samples is due mainly to coordination of titanium on the surface of ZrO2. It is generally accepted that isolated Ti(IV) in tetrahedral form are considered the most active species in epoxidation reaction [1–4,11]. Based on these facts, the effect of fluorination on increasing the epoxidation activity of F–Ti–ZrO2 and O–F–Ti–ZrO2 can be explained by the presence of isolated Ti(IV) in tetrahedral form.

The increase in epoxidation activity after alkylsilylation can be explained on the basis of an increase in the hydrophobicity of O–F–Ti–ZrO2 and F–Ti–ZrO2 catalysts. When the substrates make an interaction to the active sites on the titanium active sites, the H2O2 will release water as a side product. The hydrophobic fluor and long carbon chains of alkylsilyl groups will prevent the water to interact with titanium active sites. If this occurs, titanium active sites will be poisoned by water molecules and it might reduce the catalytic activity.

In order to check the regenerability of the catalyst, the recovered and dried F–Ti–ZrO2 was reused in fresh 1-octene and aqueous H2O2. A negligible decrease in the amount of epoxide could be seen. This suggests that epoxide formation does not occur from any leached Ti species. Although the turnover number (TON), the molar ratio of the epoxide to the loaded Ti, was less than one for the reaction with Ti–ZrO2, O–F–Ti–ZrO2 gave a TON of ca. 8, indicating catalytic action of the Ti species (see Fig. 5).

4. Conclusion

The results described above indicate that the catalytic properties of TiO2–ZrO2 (Ti–ZrO2) fluorinated TiO2–ZrO2
(F–Ti–ZrO₂) and alkylsilylated F–TiO₂–ZrO₂ (O–F–Ti–ZrO₂) exist due to the presence of titanium active sites on their surface. The increases in catalytic performance of F–Ti–ZrO₂ and O–F–Ti–ZrO₂ were brought about by fluorination and alkylsilylation processes of Ti–ZrO₂. It is demonstrated that the fluorination can change the coordination of Ti active sites from octahedral to tetrahedral and also increase the hydrophobicity of the catalyst. Alkylsilylation on the other side has absolutely increased the catalyst hydrophobicity. As expected, the catalytic activity of F–Ti–ZrO₂ increases significantly in the epoxidation of 1-octene with aqueous hydrogen peroxide. In conclusion, the high activity of O–F–Ti–ZrO₂ can be considered as the influence of its hydrophobicity and also nature of the active sites on their surface.

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Surface structure of alkylsilylated HZSM-5 as phase-boundary catalyst

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ABSTRACT: The need for cleaner environment concerns motivates the development of more efficient catalytic system. Based on this consideration, recently a novel catalyst named "Phase-boundary catalyst", a bimodal amphiphilic solid catalyst, was proposed. It was demonstrated that the catalytic system containing phase-boundary catalyst required neither stirring to make an emulsion nor addition of a co-solvent to make a homogeneous solution to drive the reaction. The driving force that has prompted this paper is to investigate the surface structure of alkylsilylated HZSM-5 as phase-boundary catalyst. Temperature Programmed Desorption (TPD) of ammonia and $^{13}$C and $^{29}$Si MAS NMR spectroscopy were used to elucidate the surface structure of alkylsilylated HZSM-5. It is suggested the addition of small amount of water to the solid particles before alkylsilylation, as a recipe to make a bimodal amphiphilic particles, is desired to enhance the acidity of HZSM-5. The enhancement of acidity might be induced by polymeric octadecylsiloxane as elucidated by $^{13}$C and $^{29}$Si MAS NMR spectroscopy.

KEYWORDS: HZSM-5; polymeric octadecylsiloxane; phase-boundary catalyst

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1 INTRODUCTION

Recently, a novel concept of "phase-boundary catalysis" (PBC) in order to utilize the immiscible liquid-liquid reaction system with solid catalysts was proposed [1-4]. In the PBC system, the bifunctional particles, containing both hydrophilic and hydrophobic regions, were placed at the phase boundary in order to catalyze the reaction without requiring an emulsion containing the catalyst by stirring. This system offers advantages in terms of ease of separation, the possibility of continuous supply of immiscible substrates and working effectively without co-solvent. Proposed model of catalyst for immiscible liquid-liquid reactions is shown in Fig. 1. The phenomenological aspects of catalytic functions in PBC and its correlation with bimodal amphiphilic character of the catalyst have been reported previously [1-6]. It was found that the highest catalytic activity under static conditions was observed when the catalyst was located at the phase boundary. We concluded that the location of catalyst in immiscible liquid-liquid system plays an important role in the reaction. However, in order to establish the PBC concept, the understanding the surface structure of phase-boundary catalyst is a conditional prerequisite and of utmost important. The emphasis of this article will therefore be to understand the surface structure of alkylsilylated HZSM-5 as a model of phase-boundary catalyst. The detail surface structures of catalyst particles is examined in more detail, focusing on clarification of the arrangement of alkylsilyl groups on the surface of particles by using Temperature Programmed Desorption (TPD) of ammonia, $^{13}$C and $^{29}$Si MAS NMR spectroscopy.

2 EXPERIMENTAL

2.1 Catalyst preparation

HZSM-5 zeolite powder was supplied by Zeolyst International (CRV 8014) and used after treatment at 450 °C under nitrogen atmosphere. Modified HZSM-5 on which the external surface was partly covered with alkylsilane was prepared by attachment of n-octadecyltrichlorosilane (OTS). This preparation method is same as given in our recent papers [1-4]. In typical experiment, in order to modify HZSM-5 with alkylsilane, the HZSM-5 powder containing water (0.5 g per 1.0 g of HZSM-5) was immersed in 10 ml toluene containing 500 μmol of n-octadecyltrichlorosilane (OTS, Aldrich) and the suspension was shaken for ca. 15 minutes at room temperature. Then, the solid was...
collected by centrifugation and dried at 110 °C for overnight. Due to the hydrophilicity of the HZSM-5 surface, addition of a small amount of water led to aggregation owing to the capillary force of water between particles. Under these conditions, it is expected that only the outer surface of aggregates, in contact with organic phase can be modified with OTS. The partly modified sample was labeled w/o-HZSM-5. Fully modified HZSM-5 (o-HZSM-5) was prepared without addition of water.

2.2 Characterization of catalysts
A TPD/R/O 1100 ThermoFinnigan was used for the temperature programmed desorption (TPD) measurements. The sample was heated at 450 °C for 2 hours and cooled down to 80 °C before passing ammonia. After saturation with ammonia, the sample was flushed with N2 to remove the physically adsorbed NH3. The temperature of desorption was increased at the rate of 10 °C/min. Due to the alkylsilyl groups are decomposed at 500 ~ 700 °C and the desorption of ammonia also occurs at this range of temperatures, the peak of the desorption of ammonia is plotted by means of subtraction of the TPD curve of ammonia desorption with TPD curve without the presence of ammonia. The MAS NMR experiments were performed using Bruker Avance 400 MHz 9.4T spectrometer. The 29Si MAS NMR spectra were recorded at 79.44 MHz using 5.5 μs radio frequency pulses, a recycle delay of 20s and spinning rate of 7.0 kHz. The 13C NMR, spectra were collected by a Cross Polarization (CP) MAS method with a 1000 μs 13C pulse and 5 s recycle delay. Both 29Si and 13C NMR chemical shifts were referred to TMS at 0 ppm.

3 RESULTS AND DISCUSSION
As shown in Fig. 2, when the w/o-HZSM-5 particles were added to a mixture of cyclohexene and water, they were feasibly located just at the liquid-liquid phase boundary, whereas HZSM-5 and o-HZSM-5 were dispersed in aqueous and organic phases respectively. To gain an idea about the nature of the active sites present in the catalysts, TPD of ammonia analysis has been made. Results of the TPD of ammonia on HZSM-5, w/o-HZSM-5 and o-HZSM-5 are presented in Fig. 3. The ammonia TPD profiles of HZSM-5 and o-HZSM-5 samples consist of two peaks at 175 °C and 475 °C. It is evident that the peaks at 175 °C of w/o-HZSM5 is shifted to a higher temperature, i.e., 280 °C, suggests that w/o-HZSM-5 possesses a stronger acidity. It was observed that the peak areas of w/o-HZSM-5 and o-HZSM-5 are similar than that
of original HZSM-5, suggesting the amount of acidity is similar. In order to explain why w/o-HZSM-5 possesses a stronger acidity, the local structure of the catalyst was elucidated by $^{13}$C and $^{29}$Si MAS NMR. Fig. 4 shows the $^{13}$C CP/MAS NMR spectra of w/o-HZSM-5 and o-HZSM-5. The intense peak at 34 ppm corresponds to the well-oriented methylene carbons. The peak is characteristic of the $^{13}$C chemical shift for the crystallite methylene carbons of the alkane chains in the all-trans conformation. The peak at 32 ppm which appears as a shoulder in the spectrum correlated to the methylene chain. Thus, the chemical-shift position of the resonance associated with the internal methylene can be used to measure the degree of order in the amorphous phase with gauche conformation in the long-chain molecules. By comparison the peak at 34 ppm (highly ordered methylene chains) and 32 ppm (less ordered methylene chains), it was observed that the chain conformation of o-HZSM-5 is more symmetrical and compact packing compared to w/o-HZSM-5 which is more irregular and loosely packed.

The close-packed conformation of the carbon chains is also evident in $^{29}$Si MAS NMR results (Fig. 5). The intense peak at -110 ppm is from Si(3SiO) in hydrolyzed OTS and from HZSM-5. In Fig. 5, three additional peaks from -50 to -80 ppm correspond to three different environments of the siloxane groups in the modified HZSM-5 [7]: (i) isolated groups that are not bound to any neighboring siloxane, (ii) terminal groups that are only bound to one neighboring siloxane, and (iii) cross-linked groups that are bound to two neighbouring siloxane. Due to the presence of small amount of alkylsilane in w/o-HZSM-5, only peaks with low intensities were observed.
Based on the above results, it is proposed that the polymeric octadecylsiloxane induced the acid strength of protonic species of HZSM-5. Note that the proton acidity could be enhanced by neighboring terminal Si-OH of polymeric octadecylsiloxane (see Fig. 5).

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Biphasic epoxidation of 1-octene with H₂O₂ catalyzed by amphiphilic fluorinated Ti-loaded zirconia

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Abstract

A series of amphiphilic fluorinated zirconia containing titanium was prepared by titanium impregnation followed by fluorination and alkylsilylation of zirconium oxide. Physical properties of the resulting samples were characterized by XRD analysis, UV–vis spectroscopy, BET surface area analysis and EDAX analysis. The effects of fluorine and alkylsilane groups on the samples were studied by the epoxidation of 1-octene with aqueous hydrogen peroxide. The epoxidation of alkenes is one of the most important methods of functionalizing simple hydrocarbons. The amphiphilic fluorinated catalysts were more active and more efficient than the conventional titania–silica and zirconia–silica mixed oxides in linear alkene epoxidation; enhanced by the presence of alkylsilane and fluorine groups in the catalysts. Modification with alkylsilane successfully induces the hydrophobic behavior of zirconia which is hydrophilic in nature; whereas fluorine was chosen for its electron-withdrawing effect which further activates the titanium active sites.

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Keywords: Fluorination; Alkylsilylation; Linear alkene epoxidation; Hydrogen peroxide; Electron-withdrawing effect

1. Introduction

Epoxides are substances of important commercial value and have found use in diverse areas. Currently, one of the most intensively researched areas of chemistry is the search for novel epoxidation methods [1–5]. Despite numerous reports in the literature, the epoxidation of terminal alkenes remains a challenge in petrochemistry. To date, liquid-phase epoxidation with hydrogen peroxide catalyzed by transition metals has been largely dominated by the use of complexes in solution [6]. However, while these homogeneous systems may be suitable for the preparation of fine chemicals or pharmaceuticals, the obvious problem of the catalyst separation and recovery has so far hampered their use in larger scale operations. In most cases, separation difficulties have been the key barrier for commercialization of delicate synthetic chemical methodologies. For this reason, the heterogeneous catalytic system offers a better alternative nowadays since it is safer, possesses higher efficiency and environmentally acceptable, eventually reducing plant maintenance and minimizes environmental harms.

Recently, we have reported a new heterogeneous system to enhance the epoxidation catalytic activity by means of fluorination and alkylsilylation of a titanium-containing catalyst [7]. The concept is based on the idea that fluorine is highly electronegative which possesses strong affinity and tendency to attract electrons from its surrounding. This is called as ‘electron-withdrawing’ effect [8,9]. Fluorine is able to attract electrons from elements nearby and thus strengthens the bond between these two elements. With this characteristic, fluorine is expected to further activate an active site by making the active site more electrophilic, easier to be attacked by nucleophile substrates like alkenes. On the other hand, alkylsilylation is aimed to induce hydrophobicity of catalyst which is a prerequisite in any epoxidation using hydrogen peroxide as oxidant [10–12]. Hence, the objective of this paper is to carefully investigate the effect of various catalyst modification conditions, such as amphiphilicity, different alkylsilane groups and effect of stirring, on the catalytic epoxidation of 1-octene. By deepening the understanding on the effects of various conditions, this study offers a new catalytic system that is more environmentally friendly, cost effective and safer.
experimental parameters, an optimized system for an efficient epoxidation reaction could be designed.

2. Results and discussion

2.1. Physical properties of catalysts

Fig. 1 shows the apparent distribution of the series of modified Ti–ZrO₂ catalysts suspended in H₂O₂ and 1-octene mixture. Only the unmodified Ti–ZrO₂ with naturally hydrophilic behavior was dispersed in the aqueous phase. This suggests that hydrophobicity is introduced to the particles upon fluorination and alkylsilylation [14]. A small amount of water was added to the dried Ti–ZrO₂ powder before mixing with alkylsilane to adjust the surface coverage of alkylsilyl groups on the particle surface. The particles were aggregated by the capillary force of water resulting in alkylsilane groups can only react with the outer surface of the aggregates. Therefore, the particles surface is amphiphilic, having both the hydrophilic and hydrophobic faces.

Fig. 2 shows the XRD patterns which demonstrate the effect of different fluorine concentration onto the zirconia structure as the support material. All samples demonstrate monoclinic phase of ZrO₂ and this crystalline structure remains unaltered upon fluorination. Unlike the widely used zeolite-based support materials which succumb to fluorination, zirconia is highly stable to modification.

Monoclinic ZrO₂ has surface area ~30 m²/g. The surface area of Ti–ZrO₂ (31 m²/g), w/o-OTS-Ti–ZrO₂ (29 m²/g), F-Ti–ZrO₂ (28 m²/g), w/o-OTS-F-Ti–ZrO₂ (28 m²/g) and w/o-CTMS-F-Ti–ZrO₂ (24 m²/g) indicating the effect of fluorination and alkylsilylation on the surface of the catalysts is negligible. The amounts of alkylsilane and fluorine groups, measured by EDAX, that were attached on the zirconia surface are relatively small. Therefore, the surface area of zirconia is not much altered. The presence of alkylsilane and fluorine components in the samples is proven in the EDAX result. The semi-quantitative EDAX analysis indicates the amounts of silicon and fluorine is ca. 2.0% and 1.2%, respectively. The local environments of titanium species which appear to be the active sites for the epoxidation reaction have been seriously investigated by UV–vis diffuse reflectance in our previous report [7]. Fluorination of the sample was found to induce transformation of some octahedral titanium framework to the tetrahedral structure resulting in a considerable enhancement in the epoxidation reaction. It is generally accepted that isolated Ti(IV) in tetrahedral form are considered the most active species in epoxidation reaction [15,16].

2.2. Catalytic epoxidation

2.2.1. Effects of alkylsilylation and fluorination

Fig. 3 demonstrates the kinetic curves of the epoxidation of 1-octene with aqueous H₂O₂ in the presence of modified Ti–ZrO₂ catalysts. Generally, modification by alkylsilane (OTS and CTMS) and fluorosilicate led to a considerable yield enhancement. In particular, the partially alkylsilylated catalysts (w/o-OTS-, w/o-OTS-F-, w/o-CTMS-F-) showed higher activities than the hydrophilic Ti–ZrO₂. OTS and CTMS are effective hydrophobic-inducing agents. By the partial modification with our method, the catalysts possess
amphiphilic behavior, containing both hydrophilic and hydrophobic regions. As a result, titanium active sites on the catalysts were exposed to both organic octene substrate and aqueous H2O2. The continuous supply of H2O2 and 1-octene to the active sites promises a higher yield. On the other hand, the positive effect of fluorination is apparent. The highly electronegative fluorine would withdraw the electrons from Ti towards the direction where the fluorine is located (Ti4+ → F-). This results in an electrophilic Ti species which is more vulnerable to the attack by π-electron clouds of the nucleophilic alkene.

2.2.2. Effect of various alkylsilane groups

Fig. 4a compares the effectiveness of OTS and CTMS alkylsilane in the epoxidation reaction. Hydrophobic-inducing alkylsilane groups have the function to attract organic substrates towards the active sites on the catalyst. However, their molecular structures have an impact on the reaction. OTS consists of 18-carbon chain whereas CTMS comprises of three methyl groups. Hence, OTS which is a bulky molecule has a steric constrain effect on the organic substrate uptake. Organic substrates are relatively more difficult to approach the active sites on the catalyst surface due to the physical barrier formed from the larger OTS molecules. Comparatively, 1-octene reached Ti active sites in a higher frequency when CTMS was used as the alkylsilane source resulting in a higher yield of product.

2.2.3. Effect of partial and fully alkylsilylation

Surface coverage of alkylsilane groups on catalyst imposes effects on the epoxidation reaction. Fig. 4b exhibits the epoxide yield obtained from the partially alkylsilylated (w/o-OTS-F-Ti–ZrO2) and fully alkylsilylated catalyst (o-CTMS-F-Ti–ZrO2). In the preparation of partially alkylsilylated catalyst, a small amount of water was added in order to prompt the aggregation between catalyst particles. The aggregation of particles allowed only the outer surface to be alkylsilylated, whereas the inner surface remained hydrophilic. The drying process after the alkylsilylation broke the aggregation generated the particles with both hydrophobic and hydrophilic surface. On the other hand, surface of the fully alkylsilylated catalyst was totally covered by hydrophobic alkylsilane, which prevent the aqueous substrates from diffusing into the titanium sites. Therefore, partial alkylsilylation is favored since it enabled a continuous supply of both organic and aqueous substrates to reach the active sites.

2.2.4. Effect of stirring

The objective of stirring in one reaction is mainly to increase the contact frequency and mass transfer between the substrates and the catalysts. Since the continuous supply of substrates to catalyst is feasible by having the amphiphility on the surface of support materials in this reaction, the necessity for stirring to enhance the product yield is greatly reduced. As shown in Fig. 5, the activity of hydrophilic Ti–ZrO2 was only appreciable under the condition of vigorous stirring. However, fluorinated catalysts gave the yield even under static condition and the product yield was increased when the reaction was carried out with stirring. As can be seen in Fig. 1, beside electron-withdrawing effect, fluorination induced certain degree of hydrophobicity to the sample resulted in the fluorinated catalysts were remained at the interphase of H2O2 and 1-octene. This provides a better chance of contact between aqueous and organic substrates. However, F-Ti–ZrO2 dropped into the aqueous phase by gravity after a few hours staying at the phase boundary. This suggesting a more effective hydrophobic-inducing agent, such as alkylsilane, is preferred for introducing hydrophobicity.
3. Conclusion

In conclusion, fluorinated Ti–ZrO₂ particles having both hydrophilic and hydrophobic surfaces were prepared by fluorination and partial alkylsilylation. The combination of fluorination and alkylsilylation of Ti–ZrO₂ were successfully gave a synergy effect on the heterogeneously epoxidation of 1-octene by aqueous H₂O₂ under optimized experimental condition.

4. Experimental

4.1. Catalyst preparation

Zirconium(IV) hydroxide [Zr(OH)₂] was used as obtained. First, tetrapropyl orthotitanate [Ti(OPr)₄] was impregnated from cyclohexanol solution into zirconium hydroxide by vigorous stirring at 343 K until cyclohexanol was dried [13]. The molar amount of Ti was 500 μmol g⁻¹ of zirconium hydroxide. The resulting dried sample was calcined at 873 K for 2 h to produce Ti–ZrO₂.

Ammonium hexafluorosilicate [(NH₄)₂SiF₆] was used as the source of fluorination. A series of ammonium hexafluorosilicate solution with different concentrations were prepared: 0.2 M, 0.4 M, 0.6 M, 0.8 M and 1.0 M. One grams of the Ti–ZrO₂ prepared above was immersed in 10 cm³ of each solution and was shaken for 15 min at room temperature. The particles were then collected through centrifugation and dried at 383 K. This sample was labeled as F-Ti-ZrO₂. The F-Ti–ZrO₂ was then further modified by alkylsilylation.

For the alkylsilylation, two alkylsilane were used. They were octadecyltrichlorosilane (OTS) and chlorotrimethylsilane (CTMS). First, a small amount of water (~50%, w/w) was added to the F-Ti–ZrO₂ to lead the aggregation among powder particles. Then, the wetted F-Ti–ZrO₂ was suspended in 10 cm³ toluene containing 500 μmol of OTS or CTMS. The suspension was centrifuged in order to remove unreacted alkylsilane and washed with toluene and ethanol. The resulting amphiphilic samples were then dried at 383 K overnight. The partially alkylsilylated particles obtained were labeled as w/o-OTS-F-Ti–ZrO₂ or w/o-CTMS-F-Ti–ZrO₂. Alkylsilylation of Ti–ZrO₂ sample without fluorination was prepared as well to give w/o-OTS-Ti–ZrO₂. The label ‘w/o-’ refers to water phase/organic phase, is to indicate the samples’ amphiphilicity.

As a reference, fully alkylsilylated hydrophobic F-Ti–ZrO₂ particles whose external surfaces were thoroughly covered with alkylsilane were also prepared without mixing water in the first step of the above described procedure for preparation of amphiphilic fluorinated catalyst; they are called o-OTS-F-Ti–ZrO₂ and o-CTMS-F-Ti–ZrO₂. Here, the label ‘o-’ refers to organic phase, is to indicate the samples’ hydrophobicity.

4.2. Characterizations and catalytic test

The samples were characterized by X-ray diffraction (XRD) on a Bruker D8 Advance instrument using Cu Kα radiation with 40 kV, 40 mA and λ = 1.5418 Å. Fluorine element in the catalysts was semi-quantitatively measured with EDAX Philips XL 40 instrument at 20 kV. Thermo Finnigan Q Surf Series BET surface area analyzer was used to analyze surface area of the catalysts.

In a typical epoxidation reaction, 50 mg of catalyst powders were placed in a glass tube with 4 ml of 1-octene (Aldrich) and 1 ml of 30% aqueous H₂O₂ (Hanns). The reaction was performed...
with stirring or without stirring at ambient temperature for 24 h. The resulting product was withdrawn and analyzed at certain interval with gas chromatograph (GC). Gas chromatograph–mass spectrometer (GC–MS) was used to verify the product.

Acknowledgement

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References

4 Bifunctional Catalyst

Atomic oxidative active site

Cluster acidic active site
TS-1 loaded with sulfated zirconia as bifunctional oxidative and acidic catalyst for transformation of 1-octene to 1,2-octanediol

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Abstract

Titanium silicalite (TS-1) loaded with sulfated zirconia as bifunctional oxidative and acidic catalyst has been synthesized at various loadings of zirconium (2–20 wt%). Structure and properties of the samples were characterized by X-ray diffraction (XRD), temperature programmed reduction (TPR), Fourier transform infrared (FTIR) and UV–vis diffuse reflectance (UV–vis DR) spectroscopy techniques. The monolayer dispersion capacity of zirconium on the TS-1 was found to be 0.65 Zr+4 nm−2 TS-1. The UV–vis DR spectroscopy showed that the tetrahedral coordination of the titanium was observed in all samples, while octahedral zirconium was only observed in the samples containing high amount of zirconium loading (10, 15 and 20 wt%). The TPR profiles suggested that the zirconium structure impregnated on the surface of TS-1 with high amount of zirconium loading (15 and 20 wt%) have a similar structure to sulfated zirconia calcined at 500 °C. Adsorption of pyridine onto the samples indicated that Brønsted acid sites are only present in samples with high sulfated zirconia loading, i.e. 15 and 20 wt%. As analyzed by XRD, the formation of Brønsted acid sites is due to the presence of disulfate species on the surface of TS-1. It has been demonstrated that samples with 15 and 20 wt% loadings of sulfated zirconia showed activity towards consecutive transformation of 1-octene to 1,2-octanediol through the formation of 1,2-epoxyoctane using aqueous hydrogen peroxide.

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Keywords: Bifunctional catalyst; TS-1; 1-Octene; Sulfated zirconia; Epoxidation; Hydrolysis

1. Introduction

A large segment of the modern chemical industry is based on selective catalytic oxidation processes [1]. More than 60% of the chemicals and intermediates synthesized via catalytic processes are the products of oxidation. Most of the oxidation processes are being carried out in the gas and liquid phases. Catalytic oxidation in the liquid phase is widely used in bulk chemicals manufacture and are becoming increasingly important in the synthesis of fine chemicals [2]. Over the last decade, titanium silicalite (TS-1) which was first synthesized by Taramasso et al. [3] in 1983 has shown excellent catalytic activity in organic oxidation reactions using hydrogen peroxide as oxidant under mild conditions. In alkene epoxidation, many works have been done to enhance the epoxide selectivity due to the industrial importance of epoxides in the synthesis of organic and pharmaceutical materials. The ability of TS-1 to catalyze a wide variety of oxidation transformations including alkenes epoxidation with 30% aqueous hydrogen peroxide has led to extensive research worldwide on the synthesis of related heterogeneous catalysts for liquid-phase oxidation [4]. The major side product of the epoxidation reaction using H2O2 is diols. It has been known that the formation of diols from epoxides is catalyzed by Brønsted acid sites. On the other hand, diols are attractive feedstocks for the fine chemical industry. At present, diols are manufactured industrially via a two-step sequence consisting of epoxidation of an olefin, followed by hydrolysis of the resulting epoxides.

Much attention has been paid to sulfated zirconia recently due to its significant catalytic activity in many hydrocarbon
conversions, such as isomerization, alkylation, acylation, esterification, etherification, condensation, nitration and cyclization [5–9]. It was shown that the catalytic activity of the sulfated zirconia is related mainly to its acid properties. Some authors have reported that the catalysts contain both Brønsted and Lewis acid sites which are responsible for the activity. Several studies have been done on the structure and activity of zirconia-loaded silica, alumina and mesoporous molecular sieves [10–15]. However, the preparation of sulfated zirconia loaded on a strong oxidative support as bifunctional oxidative and acidic catalyst, for the consecutive reaction of alkenes to diols through the formation of epoxides has never been reported. In this study, TS-1 loaded with sulfated zirconia has been synthesized and used as bifunctional oxidative and acidic catalyst in which the Ti atoms in TS-1 acts as oxidative acid sites while sulfated zirconia deposited on the surface of TS-1 acts as Brønsted acid sites. The effect of zirconium loading on the structure and properties of the catalysts was investigated. The catalytic activity was examined in the consecutive transformation of 1-octene to 1,2-octanediol through the formation of 1,2-epoxyoctane on the surface of TS-1 acts as Brønsted acid sites. The catalytic activity was investigated in the consecutive transformation of 1-octene to 1,2-octanediol through the formation of 1,2-epoxyoctane using aqueous hydrogen peroxide as oxidant.

2. Experimental

2.1. Preparation of sample

TS-1 containing 1 mol% of titanium was prepared according to a procedure described earlier [3,16]. TS-1 loaded with sulfated zirconia (SZ) was prepared by the wet impregnation method. The TS-1 was added into a solution of zirconium sulfate hydrate [Zr(SO4)2·4H2O] in water. The mixture was stirred at room temperature for 3 h, followed by evaporation of the solvent at 100 °C. The solid was dried at 100 °C for 24 h and calcined at 500 °C for 7 h. The resulting sample was denoted as XSZ/TS-1, in which X is the percentage of zirconium in the sample. For control, bare sulfated zirconia (SZ500) was prepared by drying of Zr(SO4)2·4H2O at 100 °C for 3 days followed by calcination at 500 °C for 7 h. Table 1 summarizes the zirconium contents of the samples and their treatment after impregnation with Zr(SO4)2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zr (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS-1</td>
<td>0b</td>
</tr>
<tr>
<td>2SZ/TS-1</td>
<td>1.8c</td>
</tr>
<tr>
<td>5SZ/TS-1</td>
<td>5.1c</td>
</tr>
<tr>
<td>10SZ/TS-1</td>
<td>9.9c</td>
</tr>
<tr>
<td>15SZ/TS-1</td>
<td>15.5c</td>
</tr>
<tr>
<td>20SZ/TS-1</td>
<td>20.3c</td>
</tr>
</tbody>
</table>

a) After the impregnation of Zr(SO4)2, the sample was dried at 100 °C for 24 h and calcined.

b) The sample was calcined at 550 °C for 5 h.

c) The sample was calcined at 500 °C for 7 h.

2.2. Characterization

All samples were characterized by powder X-ray diffraction (XRD) for crystallinity and phase content of the solid materials, using a Bruker Advance D8 diffractometer with the Cu Kα (λ = 1.5405 Å) radiation as the diffracted monochromatic beam at 40 kV and 40 mA. The pattern was scanned in the 2θ ranges between 20° and 40° at a step 0.02° and step time 1 s. UV–vis DR spectra were recorded under ambient conditions using a Perkin-Elmer Lambda 900 UV/VIS/NIR spectrometer. The spectra were monitored in the range of 190–600 nm. Temperature programmed reduction (TPR) experiments were performed using a TPDRO 1100 Thermo Quest CE instrument. The sample (0.05 g) was pre-treated in a nitrogen flow at the rate of 30 ml min−1 at 500 °C for 1 h and cooled down to 100 °C. The reduction analysis was performed by heating the sample from 100 up to 900 °C at a rate of 10 °C min−1 in a flowing mixture of 5% hydrogen in nitrogen H2/N2 at the rate of 25 ml min−1. Infrared (IR) spectra of the samples were collected on a Shimadzu Fourier Transform Infrared (FTIR) spectrometer, with a spectral resolution of 2 cm−1, scans 10 s, at temperature 20 °C. For acidity evaluation, the wafer of the sample (10–12 mg) was prepared and locked in the cell equipped with CaF2 windows and evacuated at 400 °C under vacuum condition for 4 h. Infrared spectra of the sample were recorded at room temperature in the hydroxyl region of 4000–3000 cm−1 and pyridine vibration region at 1700–1300 cm−1.

2.3. Catalytic testing

The catalyst performance was tested in the epoxidation of 1-octene using aqueous H2O2 (30%) as oxidant. The reaction mixture containing 1-octene (8 mmol), H2O2 (15 mmol) and acetonitrile (10 g) as solvent was put in a round bottom flask equipped with a condenser. The catalyst (0.05 g) was then added to the solution. The reaction was carried out in an oil bath under stirring at 70 °C. The products of the reaction were analyzed by a Hewlett-Packard 6890 N gas chromatograph using an Ultra-1 column and a Hewlett-Packard GC-MSD instrument using an HP5 column.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the XRD patterns of the SZ500 and SZ/TS-1 samples. It is shown that no diffraction lines for tetragonal or monoclinic phases of zirconia are observed indicating that the S regimes are highly dispersed on the surface of TS-1. It is found that the MFI structure of TS-1 was maintained after the sulfated zirconia (SZ) loading. However, the XRD peak intensities of TS-1 decreased when the loading amount of the SZ was increased. This might be due to the decrease in the percentage...
amount of TS-1 in the samples as the loading amount of the SZ increased.

The monolayer coverage of ZrO_2 can be determined from the plot of the diffraction line intensity of TS-1 at 2θ = 23° versus loading amount of zirconium on the samples as shown in Fig. 2. The diffraction line intensities of 2SZ/TS-1 and 5SZ/TS-1 were similar to those of the parent TS-1 and are significantly lower for 10SZ/TS-1, 15SZ/TS-1 and 20SZ/TS-1. Hence, a horizontal line was found for low SZ loadings and another straight line with a tangent can be drawn for higher SZ loadings. The interception of the two lines was found at 6 wt% of SZ loading which is equal to 0.65 Zr^{4+} \text{nm}^{-2} \text{TS-1}. This value corresponds to monolayer dispersion capacity of zirconium on the TS-1.

3.2. Infrared spectroscopy

The infrared spectra of zeolite lattice vibration between 1400 and 400 cm\(^{-1}\) are depicted in Fig. 3. According to Flanigen [17], the absorption bands at around 1100, 800 and 450 cm\(^{-1}\) are lattice modes associated with internal linkages in SiO_4 (or AlO_4) tetrahedral and are insensitive to structural changes. The absorption bands at around 1230 and 547 cm\(^{-1}\) are characteristic of the MFI type zeolite structure and are sensitive to structure changes. All samples showed a band at around 970 cm\(^{-1}\). The vibrational modes at around this frequency may be the result of several contributions, i.e. the asymmetric stretching modes of Si–O–Ti linkages, terminal Si–O stretching of SiOH–(HO)Ti “defective sites” and titanyl [Ti\text{O}] vibrations. However, this band can be attributed to the titanium in the framework, since silicalite,
a Ti-free zeolite, did not show any band at around this frequency [18–21]. In addition, impregnation of silicalite with Ti (sample Ti/silicalite) gave rise to no band around 970 cm$^{-1}$. Therefore, it is concluded that the TS-1 sample contains Si–O–Ti connections. There is no band shifting or additional band observed after impregnation of zirconium sulfate on TS-1. This finding suggests that both the MFI structure and titanium framework were still maintained after loading of SZ.

3.3. UV–vis diffuse reflectance spectroscopy

As shown in Fig. 4, an absorption band at around 210 nm was observed in the spectra of SZ/TS-1. This band is attributed to ligand-to-metal charge transfer not only associated with isolated Ti$^{IV}$ framework sites (between O$^{2-}$ and the central Ti(IV) atoms) in tetrahedral coordination but also with isolated Zr$^{IV}$. This is supported by the fact that the impregnation of HZSM-5, a Ti-free aluminosilicalite, with zirconium sulfate (SZ/HZSM-5) also showed a band at around 210 nm. The second band at lower energy of about 230 nm is attributed to zirconium species in an octahedral coordination [3,22].

Fig. 4 displays UV–vis DR spectra of SZ500 and SZ/TS-1 catalysts. The UV–vis DR spectrum of SZ500 indicates the existence of a shoulder band at around 210 nm and a sharp band centered at 230 nm. A single absorption band at 210 nm was observed in the spectrum of SZ/TS-1 containing low amounts of zirconium (2, 5 and 10 wt%), while a band at 225 nm was observed in the case of 15SZ/TS-1 and 20SZ/TS-1. The decrease in intensity of the band at 210 nm with an increase in SZ loading (up to 15 wt%) suggests that tetrahedral titanium species in the TS-1 was covered by SZ. This implies that as the amount of SZ loading increases, concentration of tetrahedral titanium species decreases.

Octahedral zirconium species, which corresponds to the peak at 230 nm, starts to appear in 10SZ/TS-1, being significantly high at higher SZ loading (Fig. 4). This finding indicates that not only SZ/TS-1 contains tetrahedral Ti but also agglomerated SZ at high zirconium loading.

3.4. Temperature programmed reduction

The TPR profiles for SZ500 and SZ/TS-1 after calcination at 500 °C are shown in Fig. 5. There is no peak of hydrogen consumed for sulfate-free zirconia, indicating that reduction did not occur in the sample. The SZ500 showed broad and sharp peaks with high intensities, starting at 500 °C and peaking at 700–720 °C and 750 °C. Similar TPR profiles with lower reduction temperatures can be observed for 15SZ/TS-1 and 20SZ/TS-1. The TPR profiles of 2SZ/TS-1, 5SZ/TS-1 and 10SZ/TS-1 showed a broad signal at reduction temperature of 500–700 °C. It is observed that both the signal intensity and reduction temperature decreased as SZ loading decreased.

According to Xu and Sachtler [23], the high temperature TPR peaks are assigned to the reduction of sulfate species in the sample to form sulfur dioxide and water. Besides sulfur dioxide, hydrogen sulfide was also evolved during treatment of sulfated zirconia with hydrogen in helium at high temperature [24]. Meanwhile, Bobricheva et al. [25] and Vera et al. [26] suggested that the peak at temperature range of...
500–600 °C is attributed to a surface process of lattice oxygen elimination (formation of anionic vacancies) and the reduction of Zr⁴⁺ to Zr³⁺ on the surface of zirconia sulfate during the hydrogenation process. It suggests that release of sulfate from the surface of sulfated zirconia occurs during these processes. Therefore, it can be concluded that all the TPR peaks at low and high reduction temperatures are attributed to desorption of sulfate species. Furthermore, TPR profiles of 15SZ/TS-1 and 20SZ/TS-1 are similar to those of SZ500, suggesting that there is no difference in the molecular structure of SZ between these samples.

3.5. Acidity

Fig. 6a shows the FTIR spectra of the SZ/TS-1 samples after evacuation at 400 °C for 4 h under vacuum. In the region of hydroxyl groups, the peak at 3745 cm⁻¹, which is assigned as silanol hydroxyl groups, can be clearly observed for samples with low loading amount of the SZ (2SZ/TS-1 and 5SZ/TS-1). This band was diminished at higher SZ loading (10-20SZ/TS-1), suggesting the SZ is located in the space/sites previously occupied by silanol groups. It is also possible that SZ contains hydroxyl groups since the peak at around 3550 cm⁻¹ corresponds to the hydrogen bonding between the hydroxyl groups (see Fig. 9).

The FTIR spectra of the SZ/TS-1 samples in the sulfate region are shown in Fig. 6a. It is shown that the spectra of 2SZ/TS-1, 5SZ/TS-1 and 10SZ/TS-1 are similar. The spectra of 15SZ/TS-1 and 20SZ/TS-1 showed an additional peak at 1370 cm⁻¹ which is assigned to νSȎ asymetric vibration [27]. It is clearly observed that the intensity of the peak was significantly high in 20SZ/TS-1 suggesting an increase in the amount of sulfate with an increase in SZ loading.

It is interesting to relate the surface coverage obtained from XRD with the νSȎ asymmetric peak at 1370 cm⁻¹ which appeared on the spectra of samples. It has been calculated from the XRD data that the monolayer dispersion of zirconium is 0.65 Zr⁴⁺ nm⁻² TS-1. It is revealed that the νSȎ asymmetric peak only starts to appear in the spectrum of 15SZ/TS-1 although 10SZ/TS-1 has the zirconium content almost double compared to the amount of zirconium monolayer dispersion capacity calculated from the XRD data which is 1.12 Zr⁴⁺ nm⁻² TS-1. It can be suggested that the νSȎ asymmetric band only becomes detectable in SZ/TS-1 that contains a double layer of SZ.

The acidity of the SZ/TS-1 catalysts was monitored by FTIR using pyridine as a probe molecule (see Fig. 6b). There were no significant changes in the hydroxyl region of the spectra of the samples after pyridine adsorption compared to that before pyridine adsorption. The presence of silanol peak after pyridine adsorption indicates that the silanol groups do not react with pyridine, indicating that the silanol groups are not acidic. The peaks at 1608 and 1444 cm⁻¹ in the spectra of 2SZ/TS-1, 5SZ/TS-1 and 10SZ/TS-1 are attributed to adsorbed pyridine bound coordinatively with Lewis acid sites. The spectra of 15SZ/TS-1 and 20SZ/TS-1 showed the additional absorption bands at 1640 and 1545 cm⁻¹ which correspond to pyridine interacting with Brønsted acid sites. The disappearance of the νSȎ asymmetric peak after the adsorption of pyridine is due to the reduction of the bond order of S=O from a highly covalent double-bond character to a lesser double–bond character; the shift of the band to a lower wavenumber was observed when a basic pyridine molecule was adsorbed on the catalysts [28].

The acidity study also indicates that SZ is responsible for the formation of Brønsted acid sites. In addition, it proves that Brønsted acid sites are present only in the samples containing double layer of zirconium, whereas samples with monolayer of zirconium do not show Brønsted acidity. Since the Brønsted acidity is only found in the sample containing octahedral zirconium (see UV–vis spectra of 15SZ/TS-1 and 20SZ/TS-1 in Fig. 4), it can be concluded that the sulfate species are bonded with octahedral zirconium and not with tetrahedral zirconium. This conclusion is supported by the model proposed by Clearfield et al. [29].

3.6. Catalytic activity

The catalytic properties of the SZ/TS-1 samples were studied in the catalytic epoxidation of 1-octene using H₂O₂ as oxidant in acetone as solvent at 70°C. The same reactions were carried out over a mechanical mixture of TS-1 and
HZSM-5 zeolite (TS-1-HZSM-5) for comparison. The amount of HZSM-5 was adjusted to match the amount of Brönsted acid in 20SZ/TS-1. As analyzed by pyridine adsorption, the concentration of Brönsted acid of HZSM-5 was 0.5 mmol g⁻¹. Theoretically, the epoxidation reaction of alkene to epoxide and the hydrolysis of epoxide to form diol are catalyzed by oxidative and acidic sites, respectively.

Fig. 7 shows the oxidation rate of 1-octene to 1,2-epoxyoctane using TS-1 loaded with sulfated zirconia using aqueous H₂O₂ as oxidant. At the beginning, the initial reaction rate of the catalysts with low zirconium loading (2SZ/TS-1, 5SZ/TS-1 and 10SZ/TS-1) was similar to that of TS-1 and TS-1-HZSM-5, whereas catalysts with high zirconium loading (15SZ/TS-1 and 20SZ/TS-1) showed considerably higher activities. However, at longer reaction time, TS-1 and TS-1-HZSM-5 showed the highest activity among the SZ/TS-1 catalysts (see Fig. 7). Meanwhile, SZ500 was totally inactive toward epoxidation. It was also observed that the catalytic activity of TS-1 was similar to that of TS-1-HZSM-5 suggesting that the epoxidation of 1-octene was not affected by HZSM-5. In order to evaluate H₂O₂ selectivity, the reaction was carried out with a similar molar amount of 1-octene and H₂O₂. It is observed that the yield of 1,2-epoxyoctane decreased with decreasing H₂O₂ after 24 h of reaction time under stirring condition compared to the system containing large excess of H₂O₂ (15 mmol) against 1-octene (8 mmol). The decrease in the molar amount of H₂O₂ and 1,2-epoxyoctane were similar (ca. 15%). This finding indicates that it is necessary to use excess amount of H₂O₂ in order to compensate the decomposition of H₂O₂ during the reaction.

As shown in Fig. 7, at the initial stage, the 15SZ/TS-1 and 20SZ/TS-1 catalysts had similar activities towards the formation of 1,2-epoxyoctane. The characterization results described in Sections 3.3 and 3.5 showed that both samples contain octahedral zirconium, sulfate species and Brönsted acid sites. In order to confirm the effect of sulfate species on enhancement of the catalytic activity, the epoxidation reaction was carried out using TS-1 containing 20 wt% of the sulfate-free zirconia. The result clearly showed that its reaction rate is similar to that of TS-1. Addition of HZSM-5, an acid catalyst, also shows insignificant change in the reaction rate. The structure of zirconium species present in the samples did not influence the catalytic activity of the parent catalyst either, since SZ500 is inactive as catalyst. Based on the above considerations, one concludes that enhancement of the epoxidation activity is not affected by the presence of the double layer of zirconium, the Brönsted acid sites or the octahedral zirconium. This suggests that the enhancement of the catalytic activity at the initial reaction rate could be attributed to the sulfate-bonded zirconia species present on the surface of TS-1 loaded with high amount of sulfated zirconia. The possible explanation for this phenomenon is described in the following paragraph.

It has been proposed that oxo-titanium species (superoxo- and hydroperoxo-titanium) are the reactive sites for olefin epoxidation reaction using H₂O₂ catalyzed by TS-1 [30,31]. The reactive oxo-titanium species in TS-1 was generated by interaction of tetrahedral titanium in TS-1 with aqueous H₂O₂ adducts. Therefore, the increase of epoxidation reaction rates in SZ/TS-1 catalysts can be explained by the rates of the formation of the reactive oxo-titanium species. The sulfate present on the surface of SZ/TS-1 probably can increase the adsorption rate of aqueous H₂O₂ onto TS-1. Consequently, the rate of the formation of oxo-titanium species increases and accordingly the production of epoxides is also increased. Meanwhile, a decrease in the activity of SZ/TS-1 samples that was observed at prolonged reaction time is probably due to the lower diffusion rate of 1-octene to the active sites inside the pore of TS-1.

The hydrolysis rate of 1,2-epoxyoctane to 1,2-octanediol using TS-1 loaded with sulfated zirconia using aqueous H₂O₂ as oxidant is shown in Fig. 8. Generally, TS-1, 15SZ/TS-1, 20SZ/TS-1 and TS-1-HZSM-5 were found to be active in the hydrolysis of 1,2-epoxyoctane although their activities are lower when compared with 20SZ/TS-1 and 15SZ/TS-1. Considering that SZ/TS-1 catalysts contain Brönsted acid sites, one expects that they are responsible for the hydrolysis of 1,2-epoxyoctane. Since the amount of Brönsted acid of 20SZ/TS-1 was higher than that of 15SZ/TS-1, its activity to hydrolyze 1,2-epoxyoctane was evidently higher as expected. It is noted that the amount of Brönsted acid in the TS-1-HZSM-5 was adjusted to be similar to that found in 20SZ/TS-1. However, the rate of the formation of 1,2-octanediol (up to 48 h) on the TS-1-HZSM-5 system was much lower and comparable with that on the low loading of SZ/TS-1 and TS-1. This indicates that highly active bifunctional oxidative and acidic catalyst may be prepared by deposition of SZ on the surface of TS-1 and cannot be achieved by mechanical mixing of TS-1 with HZSM-5.
Fig. 8. The oxidation rate of hydrolysis of 1,2-epoxyoctane using TS-1 loaded with sulfated zirconia. All reactions were carried out in acetone as solvent at 70 °C.

Since the size of Zr⁴⁺ (ca. 0.1 nm), the source of SZ sites, is smaller than the size of the pore entrance of TS-1 (0.5 nm), the Zr species should be attached to the internal and external surfaces. As described in Section 3.5, it is possible that the SZ is located in a place where the silanol groups of TS-1 were previously positioned. Based on this consideration, it seems that SZ is effectively located close to Ti active sites, since the epoxide immediately reacts with SZ acid active site to hydrolyze the epoxide. This consecutive reaction is more difficult to occur efficiently over the TS-1-HZSM-5 catalytic system since the epoxide must diffuse to acid sites of HZSM-5 which are predominantly located in its pore. On the basis of these results, a model of the bifunctional oxidative and acidic catalytic system for consecutive reaction of 1-octene to 1,2-octanediol is proposed (see Fig. 9).

4. Conclusion

Bifunctional oxidative and acidic catalysts have been successfully prepared by the dispersion of sulfated zirconia on the TS-1 at high zirconium loading up to double layer zirconium, i.e. 1.3 Zr⁴⁺ nm⁻² TS-1. The catalysts have oxidative site due to titanium located in the framework of silicalite, while octahedral zirconium containing sulfate as Brønsted acidic sites. It has been demonstrated that samples with 15 and 20 wt% loadings of sulfated zirconia have shown the activity toward the consecutive transformation of 1-octene to 1,2-octanediol through the formation of 1,2-epoxyoctane using aqueous hydrogen peroxide.

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References

ENHANCEMENT OF CATALYTIC ACTIVITY OF TITANOSILICALITE-1 – SULFATED ZIRCONIA COMBINATION TOWARDS EPOXIDATION OF 1-OCTENE WITH AQUEOUS HYDROGEN PEROXIDE

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Abstract
Titanosilicalite-1 (TS-1) in combination with sulfated zirconia efficiently catalyzes the epoxidation of 1-octene with aqueous hydrogen peroxide. The presence of both octahedral zirconium and sulfate species in the catalysts enhances the epoxidation rates.

Keywords: Titanosilicalite-1, sulfated zirconia, epoxidation

INTRODUCTION
Epoxides are becoming important useful commercial products in the area of petrochemical and fine chemical industries. Many efforts have been made to facilitate the production of epoxides, which include the use of catalysts in the production processes. The breakthrough was achieved by Taramasso in 1983 who reported the preparation and catalytic activity of titanosilicalite-1 (TS-1) [1]. TS-1 represents an important change since it has shown interesting catalytic properties in alkene epoxidations with hydrogen peroxide as the oxidant. Compared to the traditional oxidation reactions, H₂O₂ as the oxidant in all the oxidations catalyzed by TS-1 has the advantage of producing environmentally...
benign water as its by-product. It has been applied to catalytic oxidation of different organic substrates, for example, epoxidation of olefins, hydroxylation of aromatics, amoximation of cyclohexanol and oxidation of alcohols [2,3]. It exhibits an excellent catalytic reactivity and selectivity in different oxidations attributed to coordination of the catalytic oxidation property in titanium and shape selectivity effects in ZSM-5 structure. However, development of the catalysts in order to increase its catalytic activity towards epoxides is still in progress, such as in catalyst preparation and modification [3,4]. Meanwhile, zirconia-silica composite prepared by sol-gel method and zirconia supported on the silica aerosil have been shown to be an active catalyst in the epoxidation of 1-octene using t-butyl hydroperoxide (TBHP) as oxidant [5,6]. Its activity is related with the structure of zirconium in the materials, i.e. coordinatively unsaturated configuration. We now demonstrate that the catalytic activity of TS-1 towards the epoxidation of 1-octene with aqueous hydrogen peroxide can be enhanced by deposition of sulfated zirconia on the surface of TS-1.

**EXPERIMENTAL**

TS-1 containing 1% mol of titanium was prepared according to a procedure described earlier by Taramasso et al. [1]. Zirconium sulfate containing TS-1 was prepared by wet impregnation method. The TS-1 was added into a solution of zirconium sulfate hydrate [Zr(SO₄)₂·4H₂O] in water. The mixture was stirred at room temperature for 3 h, followed by evaporation of the solvent at 100°C. The solid was then dried at 100°C for 24 h and calcined at 500°C for 7 h. The resulting sample was denoted as XZS/TS-1, in which X was the percentage of zirconium in the sample. For comparison, unsulfated zirconia impregnated TS-1 (sample 20Zr/TS-1, Zr=20 wt.%) was prepared by impregnation of TS-1 with zirconium isopropoxide from its hexane solution at room temperature. Then, the zirconium isopropoxide was hydrolyzed followed by drying at 100°C and calcination at 500°C for 7 h. Sample ZS500 was prepared by drying of zirconium sulfate hydrate at 100°C for 3 days followed by calcination at 500°C for 7 h.

All samples were characterized by powder X-ray diffraction (XRD) for crystallinity and phase content of the solid materials, using Bruker Advance D8 Diffractometer with the CuKα (λ=1.5405 Å) radiation as the diffracted monochromatic beam at 40 kV and 40 mA. Infrared (IR) spectra of the samples were collected on a Shimadzu Fourier Transform Infrared, with a spectral resolution of 2 cm⁻¹, scanned every 10 s at 20°C. For the acidity study, the wafer of the sample (10-12 mg) was prepared and locked in the cell equipped with CaF₂ windows, and evacuated at 400°C under vacuum for 4 h. Pyridine was adsorbed at room temperature. Diffuse reflectance UV-visible (UV-vis DR)
spectra were recorded under ambient conditions on a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer. The spectra were monitored in the 190 – 600 nm range and Kubelka-Munk axis.

The catalyst performance was tested in the epoxidation of 1-octene using hydrogen peroxide (30%) as an oxidizing agent. The reaction mixture, i.e. 8 mmol of 1-octene, 15 mmol of H₂O₂ in 10 gram acetone as solvent and 0.8 mmol of cyclooctane as an internal standard were put in the round bottom flask equipped with a condenser. An amount of 0.05 g catalyst was then added into the solution. The reaction was carried out in an oil bath with stirring at 70°C. The products of the reaction were analyzed by Hewlett Packard Model 6890N gas chromatograph using Ultra-1 column and Hewlett Packard GC-MSD using HP5 column.

RESULTS AND DISCUSSION

Zirconium sulfate (ZS) at various contents was dispersed on TS-1. The XRD pattern of all the ZS/TS-1 samples showed that diffraction lines for tetrahedral or monoclinic phases of zirconia were not observed, which indicated that the ZS was highly dispersed on the surface of the TS-1. It is found that the MFI structure of TS-1 was still maintained after ZS loading (data not shown). However, the XRD peak intensities of TS-1 decreased as the loading amount of the ZS increased. This might be due to the decrease in the percentage amount of the TS-1 in the samples as the loading amount of the ZS increased. The monolayer coverage of zirconium can be determined from the graph of the diffraction line intensity of TS-1 at 2θ=23° vs. loading amount of zirconium on the samples. The diffraction lines of samples 2ZS/TS-1 and 5ZS/TS-1 showed similar intensities compared to the parent TS-1, while samples 10ZS/TS-1, 15ZS/TS-1 and 20ZS/TS-1 showed lower intensities. Hence, a horizontal line was found for low ZS loading and another straight line can be drawn for higher ZS loading. The intercept of the two lines occurred at the value 0.65 Zr⁴⁺/nm² TS-1, which is equal to 6 wt.% This value corresponds to the value for monolayer dispersion capacity of zirconium on the TS-1.

Figure 1a shows the IR spectra of the ZS/TS-1 samples after evacuation at 400°C for 4 h in vacuum. In the region of hydroxyl groups (4000-3000 cm⁻¹), the peak of silanol groups at 3745 cm⁻¹ still can be observed for samples with low loading amount of the ZS (2ZS/TS-1 and 5ZS/TS-1). However, the peak disappeared for samples with higher ZS loading (10-20ZS/TS-1). This finding suggests that the monolayer coverage of the ZS on the TS-1 is in the range of 5 to 10 wt.% of zirconium (0.57 to 1.12 Zr⁴⁺/nm² TS-1), in which all silanol groups or surface of TS-1 have been covered with ZS with the maximum amount of 1.12 Zr⁴⁺/nm² TS-1. The FTIR spectra of the ZS/TS-1 samples in the
ranges of 1700 – 1300 cm⁻¹ (Fig. 1b) show that samples 2ZS/TS-1, 5ZS/TS-1, and 10ZS/TS-1 exhibit a similar pattern, without the peak assigned for sulfate vibration. However, samples 15ZS/TS-1 and 20ZS/TS-1 showed additional peaks at 1370 cm⁻¹, assigned for asymmetric \( \nu_{\text{S=O}} \), confirming the presence of sulfate species [7]. In addition, the intensity of this peak was significantly higher in sample 20ZS/TS-1, in which the amount of sulfate increased as ZS loading increased.

![FTIR spectra](image)

**Fig. 1.** FTIR spectra of the samples: (a, b) after evacuation at 400°C for 4 h in vacuum, (c, d) after pyridine adsorption and evacuation at 150°C for 1 h
It is interesting to relate the surface coverage of zirconium sulfate from the XRD finding with that of the IR spectroscopy. The XRD data found that the monolayer dispersion was 0.65 Zr⁴⁺/nm² TS-1, while IR data had shown that the asymmetric \( \nu_{\text{S=O}} \) appeared on sample 15ZS/TS-1 (1.76 Zr⁴⁺/nm² TS-1), but not for sample 10ZS/TS-1 (1.12 Zr⁴⁺/nm² TS-1). At the value of 1.12 Zr⁴⁺/nm² TS-1, the asymmetric \( \nu_{\text{S=O}} \) did not appear although this sample had almost double the zirconium content compared to the monolayer dispersion capacity obtained from the XRD data i.e. 0.65 Zr⁴⁺/nm² TS-1. The asymmetric \( \nu_{\text{S=O}} \) only started to appear in samples at 1.76 Zr⁴⁺/nm² TS-1, which contained more zirconium than that of double monolayer capacity. It can be suggested that the second layer coverage will be formed after the formation of monolayer on the solid support. Therefore, it can be proposed that the asymmetric \( \nu_{\text{S=O}} \) started to appear on samples of ZS/TS-1 that contained double layer of ZS which was equal to 1.3 Zr⁴⁺/nm² TS-1.

The spectra of the sample after pyridine adsorption in the region of hydroxyl groups are shown in Fig. 1c. There were no significant changes of the spectra as compared to that before pyridine adsorption. The silanol peak was still present after pyridine adsorption, indicating that the silanol groups did not react with pyridine. It is therefore concluded that the silanol groups are not acidic. In the regions of pyridine and sulfate as displayed in Fig. 1d, samples 2ZS/TS-1, 5ZS/TS-1 and 10ZS/TS-1 showed similar peaks at 1608 and 1444 cm⁻¹. These bands appeared when adsorbed pyridine bound coordinatively with Lewis acid sites in which these samples have similar amount of Lewis acid sites. These results indicated that zirconium was not responsible for the formation of Lewis acid sites. Meanwhile, samples 15ZS/TS-1 and 20ZS/TS-1 showed the absorption bands at 1640 and 1545 cm⁻¹, which corresponded to pyridine interacting with the Brönsted acid sites, beside bands at 1608 and 1444 cm⁻¹ characteristic for Lewis acid sites. In addition, the peak for asymmetric \( \nu_{\text{S=O}} \) disappeared after the adsorption of pyridine, indicating that the S=O was bound to pyridine. This finding suggests that the S=O acted as an active acid site. It also indicates that ZS was responsible for the formation of Brönsted acid sites and they were only present in samples containing a double layer of zirconium, whereas samples with a monolayer of zirconium did not show Brönsted acid sites. It is therefore concluded that sulfate can only bond with zirconia at the double layer of zirconium.

The UV-Vis DR spectrum of sample ZS500 indicated the existence of a shoulder band at around 210 nm and a sharp band centered at 230 nm (data not shown). A single absorption band at 210 nm can be observed on samples ZS/TS-1 containing low amount of zirconium (2, 5 and 10 wt.%), while a band at 225 nm was observed on samples 15ZS/TS-1 and 20ZS/TS-1. The band at around 210 nm is assigned for zirconium or titanium with tetrahedral coordination. The second band at lower energy at about 230 nm is attributable
to zirconium species in an octahedral coordination. The IR and UV-Vis DR data showed that both sulfate and octahedral zirconium species can only be observed on the samples containing double layer zirconium. From these, we can conclude that sulfate species bonded with the octahedral zirconium species and not with tetrahedral zirconium species. Clearfield et al. [8] have proposed a model that allowed for the formation of Brönsted acid sites on sulfated zirconia containing octahedral zirconium species after heating at 300°C.

All samples were tested as catalysts in 1-octene epoxidation using H₂O₂ as oxidant at 70°C. Figure 2 shows the rate of the formation of 1,2-epoxyoctane over various ZS/TS-1 samples. It can be seen that samples with low zirconium loading (2ZS/TS-1, 5ZS/TS-1 and 10ZS/TS-1) did not show any significant changes to the rate of reactions towards the formation of 1,2-epoxyoctane compared with TS-1 and ZrO₂/TS-1. However, remarkably higher activities were shown by samples at higher zirconium loading, ZS15/TS-1 and ZS20/TS-1. In addition, the 1,2-octanediol as by-product was observed, due to Brönsted acid sites present in the samples. This lowered the selectivity towards 1,2-epoxyoctane.
To determine the factor that influenced the enhancement of the catalyst activities, several experiments have been conducted. Higher activities were observed on samples ZS15/TS-1 and ZS20/TS-1. The characterization results showed that both samples contained high zirconium loading, Brønsted acid sites, octahedral zirconium, and sulfate species. However, from the catalytic testing, it was shown that the TS-1 containing high loading of zirconium without sulfate species (sample ZrO/TS-1) showed similar reaction rates with TS-1 itself, while the addition of HZSM-5 zeolite that contained Brønsted acid sites did not show significant changes of reaction rates. The structures of zirconium species present in the samples also did not influence the catalytic activity of the parent catalyst. When ZS500 was used as a catalyst without TS-1, no epoxidation product was obtained. Thus, high zirconium loading, Brønsted acid sites, octahedral zirconium containing ZS/TS-1, and ZS were not directly contributing to the enhancement of the catalytic activity. Therefore, it is suggested that the enhancement of its catalytic activity can be attributed to the sulfate-bonded zirconia species present in the surface of TS-1.

For olefin epoxidation reaction using \( \text{H}_2\text{O}_2 \) catalyzed by TS-1, the reactive sites are oxo-titanium species (superoxo- and hydroperoxo-titanium) [9]. The reactive oxo-titanium species in TS-1 were generated by the interaction of tetrahedral titanium (tetrapodal or tripodal) in TS-1 with aqueous \( \text{H}_2\text{O}_2 \) adducts. It was also reported that solvent acetone retarded the formation of oxo-titanium species [9]. Therefore, in this study, the increase of epoxidation reaction rates using ZS/TS-1 catalysts can be explained by the rates of the formation of the reactive oxo-titanium species. It is known that TS-1 has hydrophobic properties, while ZS has hydrophilic properties. The sulfate present on the surface of ZS/TS-1 probably can increase the adsorption rate of aqueous \( \text{H}_2\text{O}_2 \) into TS-1. Consequently, the rate of the formation of oxo-titanium species increased and accordingly the production of epoxides are also increased.

REFERENCES

Preparation and characterization of bifunctional oxidative and acidic catalysts Nb$_2$O$_5$/TS-1 for synthesis of diols

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Abstract

Bifunctional oxidative and acidic catalyst was prepared by incorporation of titanium ion (Ti$^{4+}$) and niobic acid in zeolite molecular-sieve. The catalysts being active both in oxidation reactions due to the presence of tetrahedral Ti$^{4+}$, and acid-catalyzed reactions due to the presence of niobic acid. Nb/TS-1 was prepared by hydrothermal synthesis of TS-1, calcination in air and subsequent impregnation of niobium into TS-1. The sample was characterized by XRD, FTIR, UV–vis DR, TPR and pyridine adsorption techniques. The XRD analysis of Nb/TS-1 revealed that the MFI structure of the TS-1 support was found to be intact upon incorporation of niobium. The infrared spectra showed that the tetrahedral titanium in the TS-1 is still remained after impregnation with niobium while based on the UV–vis DR result, the niobium species are in the octahedral structure. On the basis TPR and infrared of hydroxyl groups results, it is concluded that niobium species interacted with the silanols on the surface of TS-1. Pyridine adsorption study shows both Brønsted and Lewis acid sites are present in Nb/TS-1. The catalytic results in the transformation of 1-octene to 1,2-octanediol through the formation of 1,2-epoxyoctane by using Nb/TS-1 indicate that the production of epoxide and diol was correlated with the presence of oxidative and Brønsted acidic sites in the catalyst.

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Keywords: Bifunctional catalyst; Oxidative site; Acidic site; Microporous materials

1. Introduction

Development of efficient catalysts is a challenge in catalysis research. One of the interesting fields is the creation of two active sites in a single material catalyst, so-called bifunctional catalysts. The catalysts are potentially active for consecutive processes. Bifunctional oxidative and acid catalysts have been prepared by incorporation of trivalent metal ions (Al$^{3+}$, B$^{3+}$, Fe$^{3+}$, Ga$^{3+}$) and titanium ion (Ti$^{4+}$) together in the framework of zeolites [1]. The catalysts being active both in the oxidation and acid-catalyzed reactions [2]. In a previous study, van Bekkum and co-workers [3] have demonstrated that bifunctional Ti–Al-beta zeolites can lead to acid-catalyzed consecutive reactions. The catalysts were active in epoxidation of alkenes to produce epoxide and diol. However, it is difficult to control the number of oxidative site together with acidic sites due to some competition between titanium and aluminium to become isomorphously substitute in the framework of zeolites. In order to overcome such problem, a new catalyst system has been designed.

This work focuses on the enhancement of the catalytic performance of bifunctional oxidative and acidic catalysts by incorporation of titanium and niobium into zeolite molecular-sieve. Titanium silicalite (TS-1) molecular-sieves have attracted much attention during the last decade because of their interesting catalytic properties in oxidation reactions [2–6]. Niobium has been loaded on the surface of TS-1 to introduce acidity. The surface acid strength of hydrated niobium oxide, namely niobic acid (Nb$_2$O$_5$·nH$_2$O) corresponds to the acid strength ($H_0$ ≤ −5.6) of 70% sulfuric acid and exhibits high catalytic activity, selectivity and stability for acid-catalyzed reactions [7,8].

In this paper, we reported the preparation and characterization of bifunctional oxidative and acidic catalyst, Nb/TS-1. Silicalite and TS-1 were prepared by direct hydrothermal syn-
thesis method, whereas Ti/silicalite and Nb/TS-1 were prepared by impregnation of titanium or niobium in the TS-1, respectively. By impregnation method, the titanium or niobium position was made to be in octahedral structure located as the extra-framework of silicalite or TS-1. The structure and properties of the catalysts were characterized with various techniques, such as X-ray diffraction (XRD), infrared (FTIR) and UV–vis DR spectroscopies, Temperature programmed reduction (TPR) and pyridine adsorption techniques. The catalytic activity of Nb/TS-1 in the epoxidation of 1-octene was significantly improved in comparison with TS-1.

2. Experimental

2.1. Preparation of samples

TS-1 was prepared according to a procedure described in the literature [4] with slight modification [9], using tetraethyl orthosilicates (Merck, 98%), tetraethyl orthotitanate, TEOT (Merck, 95%) in isopropyl alcohol, tetrapropylammonium hydroxide (Merck, 20% TPAOH in water), and distilled water. The gel was charged into a 150 ml autoclave and heated at 175 °C under static condition. The material was recovered after 4 days by centrifugation and washed with excess distilled water. A white powder was obtained after drying in air at 100 °C overnight. Silicalite was synthesized by using the same procedure without the addition of TEOT. The calcination of sample to remove of the template was carried out in air at 550 °C for 5 h with temperature rate 1 °C min⁻¹. Ti/silicalite and niobium silicalite (1 wt.%) were prepared by impregnation technique using TEOT as a precursor. About 0.99 g of silicalite was added into the solution of TEOT (0.0502 g) in isopropanol (50 ml) with stirring. The mixture was stirred for 4 h at 80 °C. The solid was recovered by slowly evaporating the alcohol at 80 °C. The solid material was then calcined in air at 550 °C for 5 h. Here, the prepared silicalite and niobium silicalite loaded with titanium oxide are denoted SIL and Ti/SIL, respectively.

Sample Nb/TS-1, TS-1 loaded with niobium oxide, was prepared by impregnation technique using niobium ethoxide Nb(OC₂H₅)₅ (Aldrich, 99.95%) precursor. TS-1 was dried in oven at 100 °C overnight. Silicalite was synthesized by using TEOT as a precursor. About 0.99 g of silicalite was added into the solution of TEOT (0.0502 g) in isopropanol (50 ml) with stirring. The mixture was stirred for 4 h at 80 °C. The solid was recovered by slowly evaporating the alcohol at 80 °C. The solid material was then calcined in air at 550 °C for 5 h. Here, the prepared silicalite and niobium silicalite loaded with niobium oxide are denoted SIL and Ti/SIL, respectively.

Sample Nb/TS-1, TS-1 loaded with niobium oxide, was prepared by impregnation technique using niobium ethoxide Nb(OC₂H₅)₅ (Aldrich, 99.95%) precursor. TS-1 was dried in oven at 200 °C for 24 h. After that, the necessary amount of niobium ethoxide was dissolved in n-hexane (Aldrich, >99%) to obtain the desired metal loading, and the required quantity of pre-dried of TS-1 was immediately added to the clear solution with stirring. The mixture was stirred at room temperature for 3 h. The solid was recovered by evaporating the n-hexane at 80 °C. The acid hydrolysis was performed by addition of 20 ml solution of 0.5 M HNO₃ in distilled water and aged overnight, followed by heating at 120 °C until dryness. The solid was then washed with distilled water for three times and finally dried at 200 °C for 24 h.

For comparison on the presence of Nb species, experiments were carried out to obtain niobium oxide and niobic acid. Niobic acid was prepared by hydrolysis of niobium ethoxide using neutral hydrolysis method, followed by calcination at 200 °C. The hydrolyzed niobium ethoxide is denoted NBO. Niobic acid was also prepared by calcination of ammonium niobic oxide at 550 °C for 3 h. The prepared particles were labeled NBO.

Titanium oxide was prepared by hydrolysis of titanium(IV) tetraethoxide (TEOT) at room temperature. The white solid was recovered by filtration, washing with water and drying at 100 °C overnight. Finally, the solid was calcined at 550 °C for 5 h. The thus-prepared particles were labeled TIO. Table 1 summarizes the chemical composition of all the above samples and preparation methods.

2.2. Characterizations

All molecular-sieves were characterized by powder X-ray diffraction (XRD) for identification of the crystalline phases in the catalysts using a Bruker Avance D8 diffractometer with the Cu Kα (λ = 1.5405 Å) radiation as the diffracted monochromatic beam at 40 kV and 40 mA. Typically, powder samples were ground and spread into a sample holder and then analyzed. The pattern was scanned in the 2θ range of 5°–50° at a step 0.020° and step time 1 s. Infrared (IR) spectra of the samples were collected on a Perkin Elmer Fourier Transform Infrared (FTIR) spectrophotometer, with a spectral resolution of 2 cm⁻¹ at temperature 20 °C by KBr pellet method. The framework spectra were recorded in the region of 1400–400 cm⁻¹. UV–visible diffuse reflectance (UV–vis DR) spectra were recorded at ambient condition on a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer. Temperature programmed reduction (TPR) experiments were performed using TPDRO 1100 Thermo Quest CE Instrument as follows. The sample (typically about 0.05 g) was pre-treated in nitrogen at a flow rate of 30 cm³ min⁻¹ at 200 °C for 1 h and cooled down to 100 °C. The reduction analysis was performed by heating the sample from 100 up to 1000 °C at a rate of 10 °C min⁻¹ and held for 5 min at 1000 °C with flowing mixture of 5% hydrogen in nitrogen (H₂/N₂) at the rate of 40 cm³ min⁻¹. For hydroxyl groups and acidity study, about 10 mg of the sample was pressed at 2–5 tonnes for a minute to obtain a 13 mm disk. The sample was introduced in the

Table 1

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Chemical composition of the samples and preparation method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb/TS-1</td>
<td>0.81 (gel)</td>
</tr>
<tr>
<td>H₂O/Nb/TS-1</td>
<td>NBO</td>
</tr>
<tr>
<td>H₂O/TS-1</td>
<td>100</td>
</tr>
<tr>
<td>Ti/SIL</td>
<td>100</td>
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<td>Ti/PSS</td>
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<tr>
<td>Ti/NaX</td>
<td>100</td>
</tr>
<tr>
<td>Ti/NaX</td>
<td>100</td>
</tr>
</tbody>
</table>

* %Ti = Ti/(Ti + Si) in the initial gel.

b %Ti = Ti/TS-1, wt. %.

Bifunctional Catalyst

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infrared cell with calcium fluoride, CaF$_2$ windows. The sample was heated at 200 °C in vacuum condition for 16 h. The infrared spectra were collected at room temperature using Shimadzu 2000 FTIR spectrometer at 2 cm$^{-1}$ resolutions. The types of acid sites were examined using pyridine as a probe molecule. Pyridine was adsorbed at room temperature for a minute, continued by desorption at 150 °C for an hour. The infrared spectra were monitored at room temperature.

2.3. Catalytic test

The catalyst performance was tested in the epoxidation of the 1-octene using hydrogen peroxide as oxidant. The reaction mixture, i.e. 8 mmol of 1-octene (Sigma, 99%), 15 mmol of H$_2$O$_2$ in H$_2$O (Scharlau, 35% extra pure) in 10 g acetone (J.T. Baker) as solvent and 0.8 mmol of cyclooctane (Fluka, >99%) as an internal standard were placed in a 25 cm$^3$ round bottom flask equipped with a magnetic stirrer and condenser. An amount 0.05 g catalyst was then added in the solution. The reaction was carried out in oil bath with stirring at 70 °C. The aliquots were sampled at regular time intervals. The products of the reaction were analyzed with an HP 6890N GC using Ultra-1 column and HP GC-MSD using HP5 column.

3. Results and discussion

3.1. Solid characterizations

Fig. 1 shows the XRD patterns of the samples tabulated in Table 1. The XRD pattern of TIO sample indicated that the structure of TiO$_2$ was rutile. There is no diffraction line was observed on the XRD pattern from sample NBA prepared by hydrolysis of niobium pentoxide, suggesting that niobic acid is fully amorphous. On the other hand, sample NBO, niobium oxide prepared by calcination of ammonium niobium oxalate at 550 °C shows splitting of the diffraction line around 2θ = 29°, indicating that the sample is crystalline niobium oxide phase (T-Nb$_2$O$_5$) with orthorhombic structure [10].

The XRD patterns of TS-1, SIL, Ti/SIL and Nb/TS-1 samples revealed that the sample contained framework structures of the MFI type zeolite [11]. For sample Nb/TS-1, the structure of TS-1 is not strongly affected by the presence of impregnated niobium. The XRD patterns show that no diffraction line assigned for crystalline phase of the niobium oxide present. This indicated that niobium was well dispersed on the TS-1. This also suggested that the niobium is present in the form of amorphous niobium oxide hydrate, since it was prepared by hydrolysis of niobium ethoxide and not calcined at temperature higher than 400 °C. In addition, the peak intensity of TS-1 is drastically decreased up to 60% after impregnation of 3.4 wt% of niobium on the TS-1. It is already known that the infrared spectrum of titanium silicalite, TS-1 is characterized by an absorption band at 1400 and 400 cm$^{-1}$ are depicted in Fig. 2. Sample NBA shows a major strong band centered at 586 cm$^{-1}$ and a shoulder band at 933 cm$^{-1}$. This spectrum is consistent with the skeletal vibration previously reported for amorphous niobic acid [12]. The spectrum of crystalline phase of niobium oxide (sample NBO) exhibits two strong bands at 615 and 850 cm$^{-1}$. The broad band at higher frequency ca. >850 cm$^{-1}$ is associated with the stretching mode of terminal Nb=O bonds (niobyl species), while the band around 600 cm$^{-1}$ can be assigned to the stretching of longer bridging Nb–O–Nb bonds.

The absorption bands at around 1100, 800 and 450 cm$^{-1}$ were three lattice modes associated with internal linkages in tetrahedral SiO$_4$ (or AlO$_4$) and are insensitive to structure changes. The absorption bands at about 1225 and 547 cm$^{-1}$ are characteristic of MFI-type zeolite associated with the particular structural assembly of the tetrahedral and are sensitive to structure changes.
However, the vibrational modes at around this frequency may be the result of several contributions i.e. the asymmetric stretching modes of Si–O–Ti linkages [14–16], terminal Si–O stretching of SiOH–(HO)Ti “defective sites” and titanyl [Ti=O] vibrations. Our TS-1 sample shows a weak band at 977 cm$^{-1}$. This band can be attributed to the titanium in the framework, since silicalite (SIL sample; contains only silica without addition of any titanium) does not show any band at around this frequency. Furthermore, sample Ti/SIL (titanium oxide loaded silicalite, 1 wt.% of Ti) also does not show the band around 960 cm$^{-1}$.

It is concluded that the TS-1 sample contains Si–O–Ti connections. No additional bands appeared after impregnation of titanium in the SIL sample.

A small band at around 970 cm$^{-1}$ assigned to the titanium ions in the tetrahedral structure is still present after impregnation of niobium (sample Nb/Ti/SIL). No additional band after impregnation of niobium into the TS-1 can be observed. This finding shows that impregnation of niobium has not effected the MFI structure of TS-1 significantly. Infrared spectroscopy technique also cannot detect the presence of niobic acid in the sample Nb/TiSIL, due to low vibration intensity and the sample contains silicon only without any addition of titanium or niobium. For the TS-1 sample, only a single strong band at 215 nm was observed. This band is attributed to ligand-to-metal charge transfer associated with isolated Ti$^{4+}$ framework sites (between O$^{2-}$ and the central Ti(IV) atoms) in tetrahedral coordination, Td. The band characteristic of octahedral extra-framework titanium was not observed, while Ti/SIL sample shows a broad band at 240 nm attributed to extra-framework titanium oxide suggesting that impregnation of niobium only produce some extra-framework titanium species. Impregnation of niobium on the TS-1 (sample Nb/TiSIL) shows a strong band at about 240 nm assigned to octahedral niobium species. Meanwhile, the band characteristic for tetrahedral titanium at about 215 nm cannot be observed due to the overlapping of this band with the band of niobium oxide that has remarkably higher intensity.

The nature and coordination of metal oxide or metal in substituted molecular-sieves can be characterized by UV–vis DR spectroscopy technique. Fig. 3 shows the UV–vis spectra of the samples. The UV–vis spectrum of NBA sample exhibits a maximum band around 295 nm and a shoulder band around 243 nm. This main band (295 nm) attributed to the charge transfer transitions O$^{2-}$ to Nb$^{5+}$, which can be associated to the energy gap between the O 2p-valence band and the Nb 4d-conductance band [12]. For TIO sample, the main band at around 340 nm and a strong band at 240 nm are observed, both assigned to the octahedral Ti (Oh). Silicalite (MFI sample) shows two bands at around 213 and 240 nm with very low intensity (0.05) (spectrum was magnified four times). These bands are not assigned to the coordination of titanium or niobium with oxygen due to their low intensity and the sample contains silicon only without any addition of titanium or niobium. For the TS-1 sample, only a single strong band at 215 nm was observed. This band is attributed to ligand-to-metal charge transfer associated with isolated Ti$^{4+}$ framework sites (between O$^{2-}$ and the central Ti(IV) atoms) in tetrahedral coordination, Td. The band characteristic of octahedral extra-framework titanium was not observed, while Ti/SIL sample shows a broad band at 240 nm attributed to extra-framework titanium oxide suggesting that impregnation of niobium only produce some extra-framework titanium species. Impregnation of niobium on the TS-1 (sample Nb/TiSIL) shows a strong band at about 240 nm assigned to octahedral niobium species. Meanwhile, the band characteristic for tetrahedral titanium at about 215 nm cannot be observed due to the overlapping of this band with the band of niobium oxide that has remarkably higher intensity.

Fig. 4 shows the TPR profiles of the samples. Sample NBA prepared by hydrolysis of niobium ethoxide then calcined at 200 °C exhibited three regions of hydrogen consumption, i.e. a negative peak at around 550 °C and positive peaks at around 875 °C and at a higher temperature above 1000 °C. The negative peak can be attributed to CO or CO$_2$ formation due to carbon residue from the niobium ethoxide that is not
Fig. 4. TPR profiles of the samples.

fully hydrolyzed. The first positive peak was attributed to the reduction of Nb$^{5+}$ to Nb$^{4+}$ in the form of Nb$_2$O$_5$ to NbO$_2$ [8,17], while for reduction of NbO$_2$ to lower oxidation state of niobium, NbO needed higher reduction temperature.

Sample Nb/TS-1 does not show any significant peak in this reduction temperature range, although the sample contains niobium. This finding is explained to be due to several factors. Low amount of niobium loading results in high dispersion of niobium on the surface of TS-1 that cause high interaction between niobium and TS-1. Pereira et al. [17] found that high dispersions promote intimate contact between the niobium and the silica surface, Nb-O-Si bonding in relation to Nb-O-Nb bonding prevailing. It also can be explained based on the electronegativity concept that the presence of silicon in the coordination sphere of niobium should increase the electronic density niobium. Thus the reduction of niobium from Nb$^{5+}$ to Nb$^{4+}$ was more difficult to occur. Recently, Mendes et al. [18] found that 20 wt.% of niobium supported on Al$_2$O$_3$ did not show any hydrogen uptake as indication of the interaction of niobium with Al$_2$O$_3$.

The hydroxyl groups and acidity of the samples were monitored by infrared technique. The wafer sample was put in the glass cell and evacuated at 200 °C for 16 h under vacuum. The infrared spectra were recorded at room temperature. Fig. 5 shows the infrared spectra of the samples in the hydroxyls region. Sample NBO does not shows any peak which indicates that crystalline niobium oxide has no acidity. Sample NBA shows the peaks at 1636, 1609, 1575, 1540, 1489 and 1448 cm$^{-1}$. The peaks at around 1540 and 1448 cm$^{-1}$ are due to Bronsted and Lewis acid sites, respectively. On the other hand, crystalline niobium oxide does not show any peak in the region of hydroxyl stretching mode of free Nb-O-H groups and hydroxyl with hydrogen bonding, respectively [12].

The types of acid sites in the samples were monitored by pyridine adsorption. Pyridine was adsorbed at room temperature after evacuation of the sample at 200 °C for 16 h in vacuum. The infrared spectra were collected after evacuation at 150 °C for an hour. Fig. 6 shows the infrared spectra of the samples in the pyridine region. Sample NBO does not show any peak which indicates that crystalline niobium oxide has no acidity. Sample NBA shows the peaks at 1636, 1609, 1575, 1540, 1489 and 1448 cm$^{-1}$. The peaks at around 1540 and 1448 cm$^{-1}$ are due to Bronsted and Lewis acid sites, respectively.

was reported recently by Braga et al. [19] for niobium oxide calcined at 800 °C.

The peak at 3743 cm$^{-1}$ disappeared as niobium was loaded on the TS-1. A small peak at 3733 cm$^{-1}$ and broad peak centered at around 3530 cm$^{-1}$ were observed in Nb/TS-1 sample. Meanwhile, a mechanical mixture of 20% NBA in TS-1 only shows a peak similar to that of TS-1 at around 3744 cm$^{-1}$ assigned for silanol hydroxyl groups. Although this mixture contains 20 wt.% of NBA, however, no peak at around 3700 cm$^{-1}$ assigned for Nb-O-H can be observed. It suggests that the amount of hydroxyl groups of Nb-OH in the sample NBA is much lower than the amount of silanol groups of TS-1. For samples Nb/TS-1, a drastic decrease of silanol species present on the surface of TS-1 indicates that there is strong interaction between niobium and TS-1 (niobium bonded with -O-Si, replaced hydrogen atom of silanol species in the TS-1). Since niobic acid does not show any peak in this region, the result clearly suggests that niobium species covered of the surface of TS-1. Therefore, deposition of niobium oxide species on TS-1 consumes surface Si-OH groups of TS-1, as consequently the silanol groups decreased.

The types of acid sites in the samples were monitored by pyridine adsorption. Pyridine was adsorbed at room temperature after evacuation of the sample at 200 °C for 16 h in vacuum. The infrared spectra were collected after evacuation at 150 °C for an hour. Fig. 6 shows the infrared spectra of the samples in the pyridine region. Sample NBO does not show any peak which indicates that crystalline niobium oxide has no acidity. Sample NBA shows the peaks at 1636, 1609, 1575, 1540, 1489 and 1448 cm$^{-1}$. The peaks at around 1540 and 1448 cm$^{-1}$ are due to Bronsted and Lewis acid sites,
Fig. 6. FTIR spectra of the samples after evacuation under vacuum at 200 °C for 16 h followed by pyridine adsorption at room temperature and evacuation at 150 °C for an hour, in the pyridine regions.

respectively. Similar finding has been reported by Morais et al. [20] for niobic acid. Niobium oxide containing TS-1 (sample Nb/TS-1) show the peaks similar to that of sample NBA. However, the intensity of the characteristic peaks for Bronsted and Lewis acid sites at around 1540 and 1448 cm\(^{-1}\) is lower than that of sample NBA. Jehng and Wachs [21] have reported the evidence of both Bronsted and Lewis acid sites in niobium oxide supported on silica, while Mendes et al. [18] only found Lewis acid sites in the silica supported niobic acid. On the contrary, in this study, a mechanical mixture of niobic acid and TS-1 only shows the peaks at around 1608, 1489 and 1447 cm\(^{-1}\), which are similar to those of sample TS-1.

3.2. Catalytic activity

The bifunctional catalyst Nb/TS-1 was tested in the epoxidation of 1-octene with aqueous H\(_2\)O\(_2\) in acetone at 70 °C. Samples NBO and NBA showed no noticeable activity toward the formation of 1,2-epoxyoctane. Consequently, there is no 1,2-octanediol observed from these reactions. TS-1 shows their activity toward the formation of 1,2-octanediol. However, Nb/TS-1 showed remarkable higher activity (four times higher in yield and selectivity for 1,2-octanediol) compared to TS-1. It suggested that TS-1 and Nb/TS-1 catalysts in this study contain Bronsted acid sites, since it is well known that the formation of 1,2-octanediol is catalyzed by Bronsted acid sites. However, from the pyridine adsorption studies, only Bronsted acid sites were observed on Nb/TS-1. It is suggested that the Bronsted acid sites might not have originated from the TS-1 catalyst itself, but rather formed during the reaction in the presence of water from the reaction mixtures. Meanwhile, the higher yield observed on Nb/TS-1 is due to the higher amount of Bronsted acid sites, which is responsible in this reaction. In addition, the induction time of the formation of 1,2-octanediol in TS-1 and Nb/TS-1 is observed after reaction for 24 and 3 h, respectively, indicating the higher reactivity of Nb/TS-1 catalyst. The titanium and niobium concentrations of the used Nb/TS-1 catalyst was determined by infrared and UV–vis DR spectroscopies. It is found that no leaching of titanium and niobium has been observed as analyzed by infrared and UV–vis DR spectroscopies, respectively.

4. Conclusion

Bifunctional oxidative and acidic catalysts was successfully synthesized by impregnation of niobic acid on the surface of TS-1(Nb/TS-1). It is demonstrated that the tetrahedral titanium species and niobic acid act as oxidative and acidic active sites, respectively. The catalytic results in the transformation of 1-octene to 1,2-octanediol through the formation of 1,2-epoxyoctane by using Nb/TS-1 indicate that the production of epoxide and diol was correlated with the presence of oxidative and Bronsted acid sites in the catalyst.

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References


Structural and Superacidity Study of Bifunctional Catalyst, Sulfated-Titanium/TS-1

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Abstract : Bifunctional oxidative and acidic catalysts are prepared in this study. The sulfated titanium silicalite is prepared by first, synthesizing the titanium silicalite (TS-1) having oxidative properties, followed by the deposition of titanium on the surface of TS-1, and finally, treatment of the solid with sulfuric acid. The structure of the solid samples are characterized by XRD, FTIR, and UV-Vis DR spectroscopy techniques, while the strength and the type of acid site are monitored by Hammet indicator and pyridine adsorption method, respectively. The results show that the MFI structure of TS-1 is maintained even after the treatment with sulfuric acid. However, a part of the tetrahedral titanium framework of the TS-1 has been expelled from the framework and becomes non-framework octahedral titanium after contacting with sulfuric acid. The acidity study by Hammet indicator indicates that sample possesses superacidic property, measured by Hammet indicator 2,4-dinitrobenzene (pKa = -14.52), in which the acid type is Lewis, from the pyridine adsorption.

Key words: superacidity, bifunctional catalyst, sulfated TS-1, Hammet indicator.

Introduction
One of the interesting fields in the area of catalysis is the creation of two active sites in a catalyst, the so-called bifunctional catalyst. One of the challenges is to design a highly functionalized catalyst by combination of oxidative and acidic sites for subsequent oxidation and acidic catalytic reactions. Bifunctional oxidative and acid catalysts have been prepared by incorporation of trivalent metal ions (Al^3+, B^3+, Fe^3+, Ga^3+) and titanium ion (Ti^4+) together in the framework of zeolites [1]. The catalysts are active both in the oxidation reactions and in acid catalyzed reactions [1,2].

Titanium silicate (TS-1) molecular-sieves have been paid much attention during the last decade because of its interesting catalytic properties in many oxidation reactions. This catalyst has very promising properties in the oxidation to produce fine chemicals. TS-1 is microporous crystalline molecular sieve having titanium (Ti) and silicon (Si) in the framework, which was first reported in 1983 [3]. It has MFI structure, obtained by substituting titanium for partial silicon in the framework (tetrahedrally coordinated titanium atoms in a silicate structure). TS-1 having similar structure to ZSM-5 is only containing Si and Ti in the tetrahedral structure, without any Al in the framework. As a result, the framework has no charge and consequently no Bronsted acidity can be observed from TS-1 sample [4].

It has been known that sulfate addition is widely used to enhance the surface acidity of the solid catalysts, known as solid superacid catalysts. The acidity of the solid superacid is stronger than that of 100% sulfuric acid, that is 
\[ \text{H}_2 \leq -12 \]. Some sulfated metal oxides and mixed metal oxides, such as SO_4^2-/ZrO_2, SO_4^2-/SnO_2, SO_4^2-/TiO_2, SO_4^2-/Fe_2O_3, SO_4^2-/SiO_2-TiO_2, and SO_4^2-/SiO_2-ZrO_2 possessed superacidity properties [5-14]. Sulfated metal oxides have also been impregnated onto silica, alumina, and porous materials [15-24]. The strong acid properties are related to the sulfate ions. The types of acid sites and some structural model have been presented and reported as either Lewis or Bronsted acids. These solid superacid has been applied as acid catalysts in the reactions such as...
Here, we studied the structure and acidity of bifunctional oxidative and acidic catalysts, prepared by treatment of the TS-1 microporous materials with sulfate ion. The tetrahedral titanium in the TS-1 acts as an oxidative site, while the acid site is created by the addition of sulfate ion. The structure and properties of catalysts are characterized using XRD, FTIR and UV-Vis DR spectroscopies. The acid strength of the solids is measured by Hammet indicators technique, while the type of acid is determined by pyridine adsorption which is monitored by FTIR technique.

**Experimental**

**Preparation of sample**

TS-1 (2% of Titanium, %mol) was prepared according to a procedure described earlier [3, 25], of TEOT in the surface of TS-1 was performed in the neutral condition by adding 10 ml of water, with stirring at room temperature for 24 hrs. The solid was dried at 100°C for 24 hrs (Ti/TS-1). The Ti/TS-1 was added slowly into the sulfuric acid solution (10 ml, 0.5 M, Merck, 99%), and stirred at room temperature for 1 hr. The solid was separated from the liquid by centrifugation, followed by washing with water until neutral pH. Finally, the solid was dried at 100°C for 24 hrs and calcined at 550°C for 5 hrs. The resulting sample was denoted as SO₄²⁻/Ti/TS-1.

**Characterization**

The solid structure was determined by using XRD, infrared and UV-Vis DR spectroscopy techniques. All molecular-sieves were characterized by powder X-ray diffraction (XRD) using reagents i.e. tetraethyl orthosiliclates (Merck, 98%), tetraethylorthotitanate (Merck, 95%) in isopropyl alcohol, tetrapropylammonium hydroxide (Merck, 20% TPAOH in water), and distilled water. The hydrothermal crystallization was carried out at 175°C under static condition in the stainless steel autoclave for 4 days.

Sulfated TS-1 was prepared by impregnation method as follows: About 1 g of TS-1 was added into 25 ml of H₂SO₄, 0.5 M under vigorous stirring at 80°C for 3 hrs. After evaporation of water, the solid was dried at 100°C for 24 hrs. The solid sample was then calcined at 550°C for 3 hrs. The sample was denoted as SO₄/TS-1.

Sulfated titanium TS-1 was prepared by impregnation of titanium on TS-1 using tetraethylorthotitanate, TEOT as precursor, followed by hydrolysis using water, and finally titanium TS-1 was treated with sulfate ion. For 1wt.% of Ti loaded TS-1, pre-dried of as-synthesized TS-1 sample (0.85 g) was added into the solution of TEOT (0.073 g, Merck, 95%) in isopropanol (10 ml, Merck, 98%). The mixture was stirred at room temperature for 3 hrs, followed by evaporation of the solvent at 80°C. The hydrolysis for the crystallinity and phase content of the solid materials using a Bruker Advance D8 Diffractometer with the Cu Kα (λ=1.5405 Å) radiation as the diffracted monochromatic beam at 40 kV and 40 mA. The sample was scanned in the 2θ range between 5° to 50° at a step 0.02° and step time 1s (scanning speed of 1.2°/min). Infrared (IR) spectra of the samples were collected on a Perkin Elmer Fourier Transform Infrared (FTIR), with a spectral resolution of 2 cm⁻¹, scans 10 s, at temperature 20°C by KBr pellet method. The framework spectra were recorded in the region of 1400 – 400 cm⁻¹. Diffuse reflectance UV-visible (UV-vis DR) spectra were recorded under ambient conditions on a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer. The acid strength of the solids were measured by Hammert indicators. The sample (0.05 g) was heated under nitrogen flow (40 cc/min) at 400°C for 15 minutes and cooled down to 200°C. The sample was taken out and added into the solution of benzene (Merck, 99%) containing Hammert indicators immediately and the color of indicator with different pKa were observed. The types of acid sites were characterized by absorbed base probe molecule. The wafer of the sample (10-
12 mg) was locked in the cell equipped with CaF$_2$ windows, and evacuated at 400°C under vacuum condition for 4 hrs. Pyridine as probe molecule was introduced into the evacuated sample at room temperature. Infrared spectra of the sample were monitored at room temperature after desorption of pyridine at 150°C for 1 hr.

Results and discussion
Structure characterization

XRD was used to characterize the structure and the crystallinity of the samples. Figure 1 shows the XRD patterns of the samples, while Table 1 shows the highest peak of each sample, at 2$\theta$ = 7.9°. Generally, all samples show similar XRD pattern characteristic of MFI structure type of zeolite. Introduction of SO$_4^{2-}$ anions into the TS-1 and titanium impregnated TS-1 (SO$_4^{2-}$/TS-1 and SO$_4^{2-}$-Ti/TS-1 samples) has insignificant effect to crystallinity of the sample, with less than 1% changes. In addition, no significant peaks shifting can be observed in all TS-1 treated samples. This finding suggests that the MFI structure of TS-1 is maintained after the introduction of SO$_4^{2-}$ and SO$_4^{2-}$-Ti. Figure 2 shows FTIR spectra of the samples. TS-1 sample show five peaks at ca. 1230, 1100, 800, 550 and 450 cm$^{-1}$, characteristic for MFI type of zeolites [26]. A peak at ca. 970 cm$^{-1}$ is observed which is characteristic for titanium with tetrahedral structure [27, 28]. The analogous sample of TS-1, the silicalite MFI containing only silica in the framework does not show any band at around this frequency. In addition, the impregnated Ti on silicalite (1wt.% of Ti) also does not show the band around 970 cm$^{-1}$, i.e. no additional band appears after the impregnation of titanium. Impregnation of SO$_4^{2-}$ and SO$_4^{2-}$-Ti into the TS-1 shows that all the characteristic peaks vibration for TS-1 is maintained with good intensities. However, the peak intensity for the tetrahedral titanium at ca. 970 cm$^{-1}$ decreased after impregnation with SO$_4^{2-}$ or SO$_4^{2-}$-Ti on TS-1, indicating that the amount of

Figure 1 : XRD pattern of the samples
tetrahedral titanium has decreased. In addition, a new peak at ca. 1384 cm\(^{-1}\) is observed, which corresponds to the asymmetric stretching vibration of the covalent S=O for SO\(_4^{2-}\) ion. This peak is considered as characteristic band of SO\(_4^{2-}\) on promoted superacid [6, 14]. This finding indicates that the MFI structure of TS-1 sample is not collapsed after the treatment with sulfuric acid in order to introduce the SO\(_4^{2-}\) anions. This observation can be seen in samples SO\(_4^{2-}\)/TS-1 and SO\(_4^{2-}\)-Ti/TS-1.

UV-Vis DR spectroscopy was used to monitor the titanium structure in the samples. The ultraviolet peak position of the Ti ion depends essentially on its coordination and on the size of extra-framework TiO\(_2\) particles whenever present in the sample. The band in the range of 190-220 nm is attributed to a charge transfer of the tetrahedral titanium (Td) sites between O\(^2-\) and the central Ti(IV) atoms, while octahedral Ti (Oh) is observed at ca. 260-330 nm [27, 29]. Figure 3 shows that, for TS-1 sample, only single high intense band at around 208 nm is observed. This band is attributable for titanium in the tetrahedral structure. This finding further support that TS-1 contains Ti in the tetrahedral structure. As for SO\(_4^{2-}\)/TS-1 and SO\(_4^{2-}\)-Ti/TS-1 samples, a medium intense band at ca. 215 - 228 nm and a shoulder band at ca. 270 - 312 nm are observed, which are characteristic for titanium with tetrahedral and octahedral structures, respectively. The intensity of tetrahedral titanium for both samples has decreased as compared...
Figure 3: UV-Vis DR spectra of the samples

to parent sample TS-1, in which the tetrahedral titanium intensity for $\text{SO}_4^{2-}\text{Ti/TS-1}$ sample is significantly higher than $\text{SO}_4^{2-}/\text{TS-1}$ sample. The decrease in the intensity of the tetrahedral titanium band followed by the formation of the octahedral titanium band clearly indicates that some of the tetrahedral titanium framework has been expelled from the framework, and becomes extraframework titanium, with octahedral structure.

The oxidation activity depends on the amount of titanium in the tetrahedral structure [27]. The purpose of deposition of the titanium in the TS-1 is to add the extraframework titanium on the TS-1 surface such that the $\text{SO}_4^{2-}$ anion only react with the titanium extraframework on the surface of TS-1 instead of tetrahedral titanium of TS-1. Thus, we would expect the spectrum of UV-Vis DR for this sample would give a band for tetrahedral titanium with similar intensity as for the TS-1. Table 1 shows the percentage of tetrahedral titanium in the samples (calculated based on the intensity of tetrahedral titanium in TS-1, in which TS-1 is taken as 100%) and also the position of the band. The results from the UV-Vis DR spectrum show that the intensity of the band for tetrahedral titanium species of $\text{SO}_4^{2-}\text{Ti/TS-1}$ sample is lower than that of TS-1 sample, and shift to the higher wavelength to about 215 nm. Meanwhile, for the $\text{SO}_4^{2-}\text{Ti/TS-1}$ sample, its intensity is much lower than that of TS-1 sample, and also shifts to the higher wavelength to about 228 nm. The shifting of the band to higher wavelength suggests that the $\text{SO}_4^{2-}$ anions has reacted with the tetrahedral titanium in both samples. However, the amount of tetrahedral titanium which has been reacted with $\text{SO}_4^{2-}$ anion is lower for $\text{SO}_4^{2-}\text{Ti/TS-1}$ sample as compared to the $\text{SO}_4^{2-}/\text{TS-1}$ sample. It indicates that for sample $\text{SO}_4^{2-}\text{Ti/TS-1}$, the $\text{SO}_4^{2-}$ anion has reacted not only with the tetrahedral titanium but also with the titanium extraframework (which is in the octahedral structure) on the surface of TS-1.

The band shifting in the range of tetrahedral titanium of the $\text{SO}_4^{2-}/\text{TS-1}$ and $\text{SO}_4^{2-}\text{Ti/TS-1}$ samples to higher wavelength at ca. 228 and 215 nm shows that the charge transfer of the tetrahedral titanium sites between $\text{O}^{2-}$ and the $\text{Ti}^{4+}$ atoms for both samples is lower than that of the TS-1. This finding indicates that the oxygen atom in the tetrahedral titanium which has charge transfer of $\text{O}(2p) \rightarrow \text{Ti}(3d)$ is bonded with the sulfur atom in the form of $\text{SO}_4^{2-}$. The electronegativity of the sulfur atom (2.58, Pauling unit) is higher than that of silicon atom (1.90, Pauling unit). Therefore, for $\text{SO}_4^{2-}/\text{TS-1}$ and $\text{SO}_4^{2-}\text{Ti/TS-1}$ samples, electron
density in the oxygen atom decreases, consequently, the charge transfer energy of O(2p) → Ti(3d) decreases, comparing to TS-1 sample. As a result, the tetrahedral titanium band shifted to the higher wavelength (lower energy) in the UV-Vis DR spectroscopy.

**Acidity studies**

The acid strength of the sample was measured by observing the changing of the color of Hammet indicators [5], when the dried solid sample was poured into the solution of the indicator in benzene. Table 2 shows the acidic strength of the samples measured by Hammet indicators. H-ZSM-5 sample is found to have an $H_0$ value around –11.35 (measured in 1-nitrotoluene), in which the strength is similar with 98% of sulfuric acid. The TS-1 sample does not show any color changing of all Hammet indicators up to the pKa = -5.6 (measured in benzalacetophenone), indicating that the samples have low acid strength. Meanwhile, the $SO_4^{2-}$/TS-1 and $SO_4^{2-}$-Ti/TS-1 samples show color changing for all Hammet indicators, including measured in 2,4-dinitrobenzene (pKa = -14.52). This result suggests that both samples contain superacidity.

The type of acid sites of the samples were monitored by pyridine adsorption after evacuation of the samples at 400°C under vacuum, followed by adsorption of pyridine at room temperature, and evacuation at 150°C for an hour under vacuum. Samples were recorded by FTIR spectroscopy at room temperature in the range wavenumber of 2000 – 1400 cm$^{-1}$. The main peaks at ca. 1450 cm$^{-1}$ and 1545 cm$^{-1}$ are characteristic for Lewis and Brønsted acid sites, respectively. While the peak at ca. 1880 cm$^{-1}$ is characteristic for vibration of the titanium silicalite framework. Figure 4 shows the spectra of the samples after evacuation at 150°C. All samples only show the peak at ca. 1445 cm$^{-1}$ which corresponds to Lewis acid sites, while the peak for Brønsted acid sites at ca. 1545 cm$^{-1}$ was not observed. This finding indicates that all samples only contain Lewis acid sites. The amount of the acid sites increase in sample $SO_4^{2-}$/TS-1 after the Ti loaded on the surface of TS-1 was treated by sulfuric acid.

It has been reported that the introduction of sulfate anions on the surface of zirconia has been found to increase the number and strength of the Lewis acid sites. It has been proposed that superacid sites of the sulfated oxides material such as zirconia is formed via oxidation of zirconia hydroxide in the presence of sulfate ion at high temperature, regardless of the types of starting materials used for sulfation [14]. It has further been suggested that such a structure may develop at the edge or corner of the metal oxide surfaces. In this study, for the samples $SO_4^{2-}$/TS-1 and $SO_4^{2-}$-Ti/TS-1, based on the characterization results especially the UV-Vis DR spectroscopy technique, the proposed structure of sulfated titanium on TS-1 is shown in Figure 5. The $SO_4^{2-}$ ion is bonded with the titanium framework and titanium extraframework.

![Image](image_url)
Bifunctional Catalyst

Conclusions
Bifunctional oxidative and superacid catalysts have been prepared. The $\text{SO}_4^{2-}/\text{TS}-1$ and $\text{SO}_4^{2-}-\text{Ti}/\text{TS}-1$ samples showed both oxidative and acidic sites. The amount of oxidative site is higher for $\text{SO}_4^{2-}-\text{Ti}/\text{TS}-1$ sample than of $\text{SO}_4^{2-}/\text{TS}-1$ sample, while the superacid strength is similar in both samples. However, creation of superacid sites caused the decrease in the oxidative sites.

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References
Synergetic Multi Reaction Center Catalyst

Oxidation of cyclohexene by lattice oxygen

Mars-van Krevelen Mechanism

Catalyst regeneration steps

$M_xO_y = \text{Nb}_2O_5$

Hydrophobic

Hydrophilic
A NOVEL DESIGN OF HETEROGENEOUS CATALYST FOR LIQUID-GAS REACTION SYSTEM WITH MARS-VAN KREVELEN TYPE MECHANISM

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ABSTRACT
The oxidation of cyclohexene with molecular oxygen, in the presence of hydrophobic niobium oxide/silica as catalysts, has been investigated. The catalysts have been prepared by impregnation of niobium penta-ethoxide on the silica surface followed by attachment of alkylsilyl groups from octadecyltrichlorosilane (ODS) on the surface with partial coverage. Cyclohexene was oxidized to 2-cyclohexen-1-ol, 2-cyclohexen-1-one and 7-oxabicyclo[4.1.0]hexane by molecular oxygen at atmospheric pressure in the presence modified Nb₂O₅/silica particles without any solvent at 70°C. These catalysts are efficient for the oxidation of cyclohexene with molecular oxygen which probably occurs with Mars-van Krevelen type mechanism. Based on these results, a catalyst design for liquid-gas reaction system is proposed.

1. INTRODUCTION
Solid-gas catalyzed-liquid reactions are often encountered in the chemical process industry, most frequently in hydroprocessing operations and in the oxidation of liquid phase organic [1-4]. In respect of the latter reaction type, the system usually has been applied for mineralization of toxic organics in wastewaters. However, synthesis of useful organic materials with this system is also one of particular field of application. Along this line, we have attempted to make an effective heterogeneous catalytic system for this application.

Recent results about the evidence for a Mars-van Krevelen type mechanism for oxidation with molecular oxygen in the liquid phase have been reported in several journals [5-7], making this system a good starting point for further extensive research on this kind of mechanism in liquid system. Those are the only reports on the liquid-phase Mars–van Krevelen mechanism-type oxidation in liquid phase system. This is interesting because by controlling the lattice oxygen diffusion, an effective catalyst for liquid-gas system could be obtained with a proper selection of oxide (as catalyst/active site).

Recently, we proposed a novel concept of “phase-boundary catalysis (PBC)” in order to utilize the immiscible liquid-liquid reaction system with solid catalysts [8-12]. In the PBC system, it was demonstrated that the bimodal amphiphilic zeolite particles could be placed at the liquid-liquid phase boundary between aqueous hydrogen peroxide and water-immiscible organic phases and act as efficient catalyst for epoxidation reaction. In this paper, it is demonstrated that the phase-boundary catalysts not only show catalytic activity in liquid-liquid boundary, but also in liquid-gas system. For this purpose, the oxidation of cyclohexene with molecular oxygen using hydrophobic niobium oxide/silica particles is chosen as a reaction model. Creating active sites which is suitable for Mars-van Krevelen mechanism is proposed in this paper.

Despite the numerous reports on selective oxidation of hydrocarbons using niobium oxide, the oxidation of alkenes by molecular oxygen using Nb₂O₅/silica system has never been reported. The use of molecular oxygen as the oxidant makes the reaction interesting from both economic and environmental points of view.

2. EXPERIMENTAL
Catalyst preparation
Silica sol with a primary particle size of 500 nm (Nissan Chemical Industries), was used after evaporation of water in order to get dry powder. Partially modified silica, whose surface was partly covered with alkylsilane, was prepared in two steps. First, niobium penta-ethoxide Nb(OC₂H₅)₅; Wako Pure Chemical) in ethanol solution was impregnated into silica powder and heated at 383 K
overnight. After this treatment, it is believed that the niobic acid (Nb₂O₅·nH₂O) is formed [12]. At this stage, the modified silica is called Nb-silica. The molar amount of Nb was 500 μmol g⁻¹ of silica. In the second step, the Nb-silica powder in water (20 wt%) was immersed in 10 cm³ toluene containing 500 μmol of n-octadecyltrichlorosilane (ODS, ShinEtsu), and the suspension was shaken for ca. 5 min at room temperature. Then, the solid was collected by centrifugation and dried at 383 K overnight. Due to the hydrophilicity of the Nb-silica, the addition of a small amount of water led to aggregation by the capillary force of water among particles. Under these conditions, it is expected that only the outer surface of aggregates, being in contact with the organic phase, could be modified with ODS. The partially modified sample was labeled as part-Nb-silica.

Fully modified Nb-silica (full-Nb-silica) was prepared as follows. ODS (500 μmol) was dissolved in a mixed solution of toluene (80 vol%) and CCl₄ (20 vol%). A dried sample of Nb-silica (1 g) was added to the solution, and the mixture was stirred overnight at room temperature. A solid sample was collected by centrifugation, washed with CCl₄ and then ethanol, and dried at 383 K overnight.

**Reaction conditions and analytical method**

Oxidation of cyclohexene was carried out in the presence of air and oxygen under atmospheric pressure. Typically, cyclohexene (2 cm³, Wako), and catalyst powder (50 mg) were placed in a glass tube, and the reaction was performed with stirring at 1000 rpm for 20 h at 70°C. Because of the presence of an appreciable amount of impurities, cyclohexene was purified by passing through column of basic alumina (Merck). The reaction products were analyzed by gas chromatography (a Shimadzu GC-14B gas chromatograph equipped with a flame ionization detector and DB-1 column) and GC/MS.

### 3. RESULTS AND DISCUSSION

As shown in Fig. 1a, in the mixture of cyclohexene and air, the catalyst exhibits an interesting activity during the catalytic oxidation of cyclohexene. The catalytic reaction was carried out in the absence of solvent at 70°C without the use of any special oxidant or co-reductant, affording 2-cyclohexen-1-ol and 2-cyclohexen-1-one as the major products. No products of the oxidation of double bond was observed in the organic phase.

When molecular oxygen was used as oxidant, a similar product selectivities were obtained and the activities were higher compared with those obtained by using air. It was observed that 2-cyclohexen-1-ol and 7-oxabicyclo[4.1.0]hexane were the major products in the conversion of cyclohexene over modified Nb-silica catalysts (Fig. 1b).

Figures 1 and 2 show the trend of the yield of the oxidation products in the presence of modified Nb-silica. The results suggest that all the part-Nb-NaY showed higher activity in liquid-gas system. Interestingly, when the reaction was performed in strictly anaerobic condition, after molecular oxygen is completely removed and replaced by bubbling Argon, and in the presence of part-Nb-silica, the oxidation products observed; were 2-cyclohexen-1-ol (8.2 μmol), 7-oxabicyclo[4.1.0]hexane (4.1 μmol) and 2-cyclohexen-1-one (0.5 μmol). None of these products were observed in the presence of only silica and without catalyst. This suggests that the oxidation of cyclohexene may occurs with Mars-van Krevelen mechanism, in which the lattice oxygens transferred from the oxide (Nb₂O₅) to yield the reaction products. This phenomenon is also supported by the fact that the amount of the oxidation product is larger than the amount of oxygen in the system.

In the system containing part-Nb-silica (see Fig. 1b), it is calculated that the amount of products (1.00 mmol) is larger than the amount of molecular oxygen (0.98 mmol). Due to the low activity of the system containing Nb-silica and full-Nb-silica, the evidence of the Mars-van Krevelen mechanism is not observed.

Silica particles are dry particles. They become hydrophobic after their surface silanols are replaced by alkylsilan groups. In order to show the hydrophobicity/hydrophilicity character of Nb-silica, part-Nb-silica and full-Nb-silica, the dispersibility of these particles in the immiscible mixture of cyclohexene and water was compared. It was observed that the part-Nb-silica particles were effectively located at liquid-liquid boundary of water and cyclohexene mixtures, whereas Nb-silica and full-Nb-silica were well-dispersed in the aqueous and organic phases respectively, due to their hydrophilicity and hydrophobicity. The reason why part-Nb-silica was effectively located at liquid-liquid boundary is due to its surface structure. Recently, it has been clarified that the methods used here for making part-Nb-silica could produce bimodal particles, i.e., one side is covered with hydrophobic alkylsilan groups and the other is kept hydrophilic [8].
Based on the above discussions, it can be proposed that the higher activity of part-Nb-Silica is due to the stabilization of liquid-gas system by bimodal amphiphilic particles as shown in Fig. 2. The use of hydrophilic catalyst (Nb-silica) decreases the wetting efficiency. Although the wetting efficiency could be increased by attachment of the alkylsilyl groups with full coverage (full-Nb-silica), the gaseous reactant is difficult to reach the catalyst surface, because it has to overcome gas-liquid and liquid-solid mass transfer resistance. According to the model, there is a path for O$_2$ to reach the niobium oxide active sites: from the gas bulk towards the “dry” catalyst surface, for which O$_2$ has to overcome only the gas-solid mass transfer resistance. This should lead to changes in catalytic properties; demonstrated by higher catalytic activity of part-Nb-silica compared to full-Nb-silica and

Fig. 1 The yield of 2-cyclohexen-1-ol, 2-cyclohexen-1-one and 7-oxabicyclo[4.1.0]hexane on the oxidation of cyclohexene using various modified Nb-silica under stirring condition at 1000 rpm. All reactions were carried out at 70°C for 20 h: 50 mg catalyst, 2 cm$^3$ cyclohexene and 11 cm$^3$ oxygen (a) and 11 cm$^3$ oxygen (b) at atmospheric pressure.
Fig. 2 The stabilization of amphiphilic solid particles containing niobium oxide as actives sites on liquid-gas (cyclohexene-O2) for oxidation of cyclohexene with Mars-van Krevelen Mechanism.

In conclusion, the results described above demonstrate the feasibility and possibility of the amphiphilic niobium oxide-silica working as catalyst for oxidation of cyclohexene with molecular oxygen with Mars-van Krevelen type mechanism.

ACKNOWLEDGMENTS

Prof. Dr. Bunsho Ohtani (Hokkaido University) and Assoc. Prof. Dr. Shigeru Ikeda (Osaka University) are acknowledged for their collaboration in the development of “Phase-boundary catalysis” concept during my stay as JSPS postdoctoral fellow (1999-2001) and COE foreign researcher (2001-2002) at Catalysis Research Center, Hokkaido University, Japan.

REFERENCES

Glossary

Biocatalysis  Catalyzed reactions where the catalyst is an enzyme.

Catalysis  A change in the rate of chemical reactions in the presence of substances (catalysts) that come into intermediate chemical interactions with the reactants, but restore their chemical composition after each cycle of the intermediate interactions. Reactions with the participation of catalysts are called catalytic.

Catalyst  A substance that, usually as a result of chemical bonding with one or more reactants, increases the rate of a chemical reaction without being consumed to any significant degree.

Consecutive reaction  A reaction in which more than one bond-breaking and/or bond-forming step occurs almost consecutively.

General acid catalysis  Catalysis in which an undissociated acid donates a proton to a reactant.

Heterogeneous catalysis  Catalyzed reactions in which the catalyst and reactants are in different phases (solid, liquid or gas).

Homogeneous catalysis  Catalyzed reactions in which the catalyst and reactants are in the same phase (solid, liquid or gas).

Lewis acid  A substance that is an electron-pair acceptor.

Rate-determining step  One step in a sequence or cycle that is the bottle-neck; all the other steps achieve virtual equilibrium.

Regenerability  Susceptibility of a catalyst to regeneration of its activity, for example, in a treatment such as burning off of carbonaceous deposits.

Selectivity  A measure of catalytic activity for one reaction relative to that for other reactions. This term is often used more or less interchangeably with “specificity” and “directivity”.

Specific acid catalysis  Catalysis in which a hydrated proton (H$_3$O$^+$) donates
a proton to a reactant.

**Specific base catalysis** Catalysis in which an OH- ion accepts a proton from a reactant.

**Substrate** Reactant.

**Support** A solid, the surface of which incorporates catalytic components. The surface of the support may be involved in catalysis, but instead may be inert.

**Turnover** Single reaction event or turn of a catalytic cycle. To demonstrate the occurrence of catalysts rather than a stochiometric reaction, the experimenter must demonstrate that the number of reactions events per catalytic site exceeds unity.

**Zeolite** A group of aluminosilicate materials, some of which occur in nature. They are widely used as catalysts and as catalyst supports.
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Scientific Biography of Hadi Nur

I grew up on a university campus in West Sumatra, Indonesia. My father, Nur Anas Djamil, was a Professor in Islamology at Institute of Teacher Training and Education (now State University of Padang) in Padang. I first became interested in chemistry one day in 1984 when I was a senior high school student. I attended an additional course in chemistry subject. This course was taught by Drs. Tahasnim Tamin, a senior lecturer at Institute of Teacher Training and Education in Padang. I was interested with the beautiful concept of chemistry that he was taught with laboratory demonstrations and analogies. This lesson also of course could not be learned without dedicated teacher that one encounters along the way.

The next important lesson came as an undergraduate in chemistry at the Institut Teknologi Bandung, Indonesia. In my three years as an undergraduate, I had chosen to do research for my final project with Dr. Harjoto Diojosubroto, Director of Nuclear Engineering Research Center, National Nuclear Energy Agency, in Bandung. He was interested in Neutron Activation Analysis (NAA) of having received his Ph.D. in hot atom chemistry. We planned a comparative study on the determination of selenium in human blood by neutron activation analysis which took me the next two years to do. He also inspired me to pursue postgraduate studies.

In September of 1993, I enrolled a new master program in material science and engineering at Institut Teknologi Bandung and was fortunate enough to work with Dr. Bambang Ariwahjoedi who was a creative lecturer and had many great ideas. Creativity is very important at that time because of lack of scientific instruments in our department. I finished a small final project in the topic of synthesis of hydroxylapatite bioceramics by means of precipitation and its characterization. I received M.Eng. with *cum laude* in 1995.

Having batted zero for my professional career up to this point, I was ready for Ph.D. research. I continued my postgraduate studies in zeolite chemistry at Universiti Teknologi Malaysia under supervision of Prof. Halimaton Hamdan. I tackled a project on the synthesis, characterization and catalytic activity of ultra-large pore of aluminophosphate molecular sieves, VPI-5, just recently successfully synthesized by Prof. Mark Davis and his co-workers. After six months experimental work, I failed to synthesize VPI-5. Everything
in my thesis comes from the last twelve months in the laboratory. Nonetheless, since we had another project on synthesis of zeolite from rice husk ash that both worked at once, I ended up with three international publications together on the study of the structure, physicochemical properties and catalytic activity of metal-substituted AlPO₄-5. I also proposed and successful in synthesizing NaA zeolite directly from rice husk and carboneceous rice husk ash. This was an incredibly intense twelve months during which I did not sleep more than five hours a night. I finally found out what independently doing good science. It was an exhilarating period. I finish my PhD project in two and half years in 1998. I continue work as a postdoctoral fellow for one year at Universiti Teknologi Malaysia. I would like to acknowledge Prof. Halimaton who have supported and encouraged me throughout all of my scientific career.

In 1999 I was fortunate enough to land a postdoctoral position with Prof. Bunsho Ohtani at Catalysis Research Center, Hokkaido University, Japan. Professor Ohtani is at least partly responsible for my career in heterogeneous catalysis. I was fortunate enough to work with Professor Ohtani who was a truly inspirational scientist and personality. He had endless capacity to produce great ideas. In two years as JSPS (Japan Society for the Promotion of Science) Postdoctoral Fellow and continued stay as COE (Center of Excellent) visiting researcher at Catalysis Research Center for a half year, we published a seminal paper on a new concept in heterogeneous catalysis termed “Phase-boundary catalysis”. I finished my postdoctoral stay which was due to the talented efforts of Dr. Shigeru Ikeda in the Ohtani group. I will always be indebted to Prof. Ohtani for showing me how to do science right. It is a debt that I can never repay, but showing new researchers the joy of chemical research is at least a small effort in this regard not to mention a lot of fun.

In May 2002, for one year, I joined the Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia as Research fellow and in 2003 I accepted my first academic position as lecturer at this university. I am very grateful having for the opportunity to work with very helpful and pleasant collaborates specifically Prof. Dr. Halimaton Hamdan, Assoc. Prof. Dr. Zainab Raml, Assoc. Prof. Dr. Salasiah Endud and Assoc. Prof. Mohd Nazlan Mohd Muhid. My research ideas such as bifunctional catalysis, amphiphilic catalysts, a new method to quantify a mixture of hexagonal MCM-41 and cubic MCM-48 mesophases by $^{13}$C CP/MAS NMR, iron-porphyrin encapsulated in poly(methacrylic) as catalysts in the oxidation of benzene to phenol were published in international refereed journals. In the future we will examine heterogeneous catalyst designs for other important chiral reactions in organic synthesis.

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