

The Design and Synthesis of Heterogeneous Catalyst Systems for Synthesis of Useful Organic Compounds

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Abstrak

Banyak sistem katalitis heterogen telah dilaporkan dan kebanyakannya, mekanisme dari sistem katalis tersebut telah dipahami dengan baik. Dalam tulisan ini, kami berusaha menggolongkan sistem-sistem katalitis heterogen yang contoh-contohnya diambil dari penelitian-penelitian yang kami lakukan dalam bidang ini. Penelitian-penelitian tersebut digolongkan ke dalam lima kelas: katalis tunggal, sistem katalis hidrofilik-hidrofobik, katalis dwifungsi dan fotokatalis. Katalis-katalis tersebut telah didisain untuk mensintesis senyawa-senyawa organik yang bermanfaat.

Kata kunci : -

Abstract

There are many different heterogeneous catalytic systems. Of most basic mechanistic features are well understood. Here an attempt will be made to classify several heterogeneous catalytic systems which contain examples from our research project in this area. Our works has been classified into five classes: single center catalyst, hydrophobic-hydrophilic catalytic system, bifunctional catalyst and photocatalyst. The catalysts have been designed for synthesis of useful organic compounds.

Keywords: -

Introduction

The name 'catalysis' was coined by Berzelius in 1836 [1]. Many types of materials can serve as catalysts. These include metals, metal compounds (e.g., metal oxides, sulfides, nitrides), organometallic complexes, and enzymes. 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].

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. Solid, heterogeneous catalysts have the advantages of ease of recovery and recycling and readily amenable to continuous processing.

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

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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.

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. Solid, heterogeneous catalysts have the advantages of ease of recovery and recycling and readily amenable to continuous processing.

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].

“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. 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. The development of heterogeneous catalyst may be regarded as an iterative optimization 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 and quantum chemistry, catalyst modeling and mechanistic simulations 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 preparation, reaction and isolation. The preparatory step of the catalyst is the most difficult step because many experimental parameters are involved.

Table 1: Homogeneous versus heterogeneous catalysis.

| | Homogeneous | Heterogeneous |
|----------------------|-------------|---------------|
| Activity | +++ | - |
| Selectivity | +++ | + |
| Catalyst Description | ++ | - |
| Catalyst Recycling | - | +++ |
| Turn Over Number | + | +++ |
| Quantity of Catalyst | ++ | +++ |

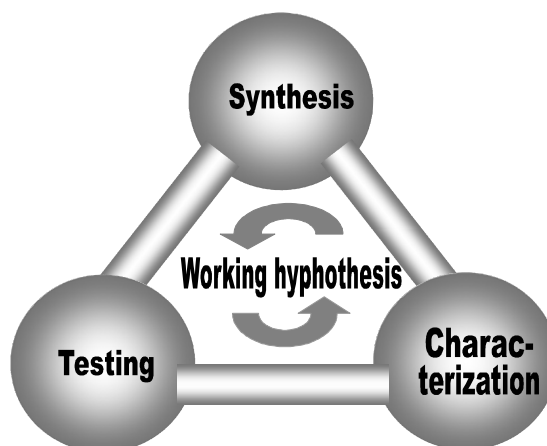


Figure 1: Schematic representation of the catalyst development cycle.

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 re-generated. The elementary rate constant for product desorption often competes with the elementary rate constant for reactant activation, leading to the Sabatier volcano curve for overall rate of reaction versus interaction strength of the intermediate reaction complexes with catalytic bonding site. There are many different catalytic systems. Of most basic mechanistic features are well understood. Here an attempt will be made to introduce several catalytic reactions in order to design a better catalyst through chemical design. The catalytic reactions are the oxidation and acid catalysis by heterogeneous catalysts. I classify our works into five classes:

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

The above classification was inspired by classification of catalytic system proposed by Prof. R. van Santen of Technische Universiteit Eindhoven [9]. The purpose of this paper is to introduce several designs of heterogeneous catalytic systems. The catalyst designs described in this paper are classified based on classification from the catalytic processes that contained examples from research that was made by the author together with his colleagues and students.

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] (see Figure 2). 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, Al atom in the framework structure has been substituted 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 dehydration 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 as my PhD research. The other examples of researches in single center catalyst system which have been developed in our laboratory are metal complexes

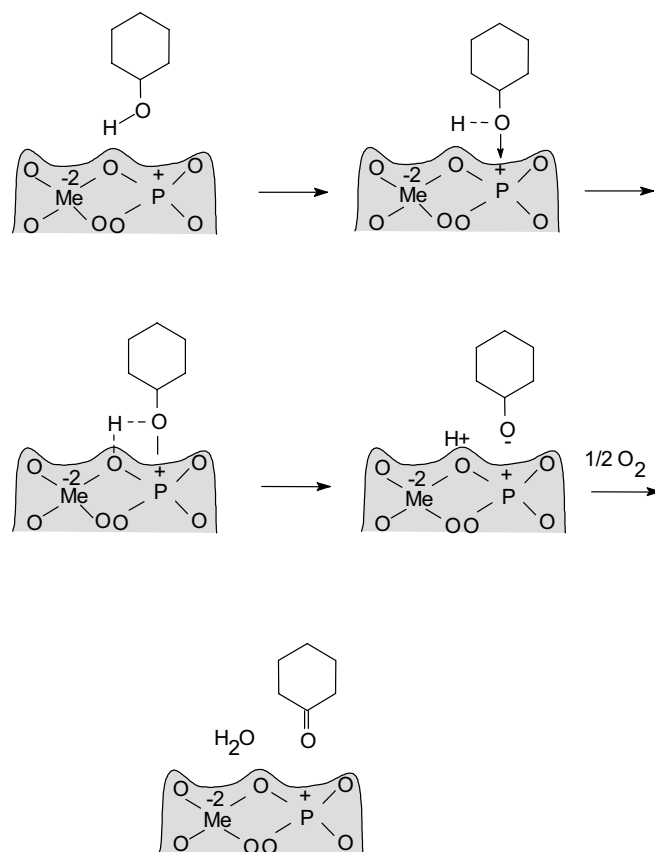


Figure 2: Proposed mechanism of dehydrogenation of cyclohexanol over a base site in MeAPO-5 [10].

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] and Ti-OMS-2 as catalyst in oxidation of cyclohexene [20,21], catalysis by zeolite beta [22,23] and modification of surface of titania by attachment of silica nanoparticle for the enhancement of epoxidation of alkene [24].

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 [25-35].

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 3 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 3. 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 3);

- 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 4 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 substrate from

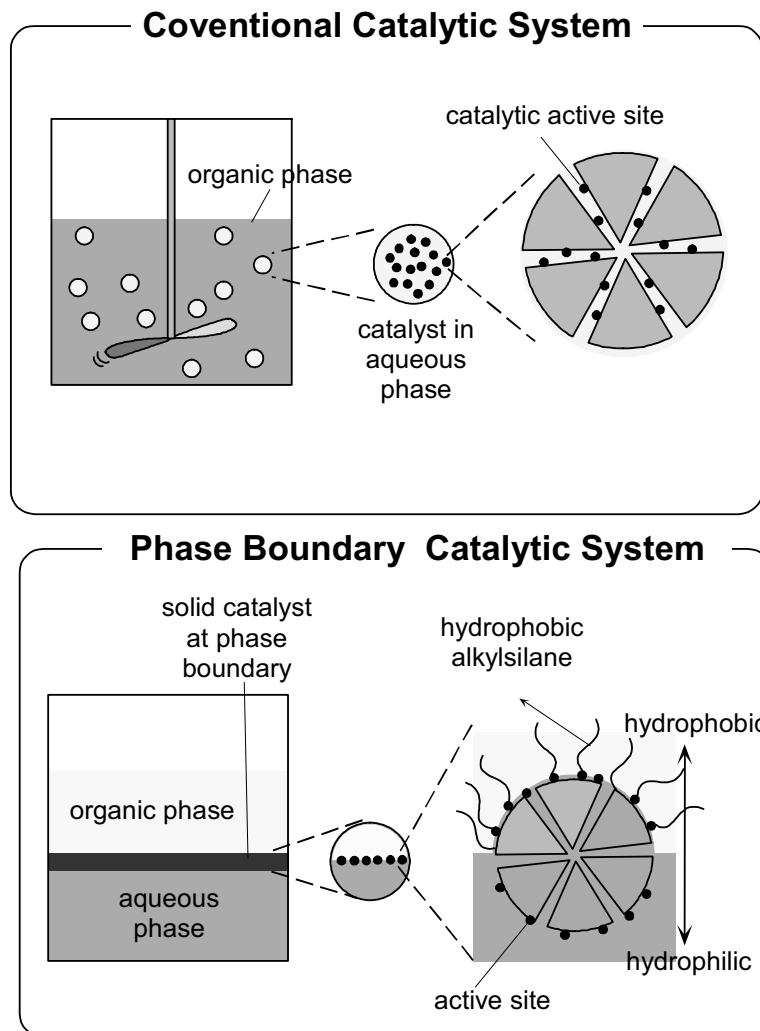


Figure 3: Schematic representation of the advantage of phase-boundary catalysis in comparison with conventional catalytic system.

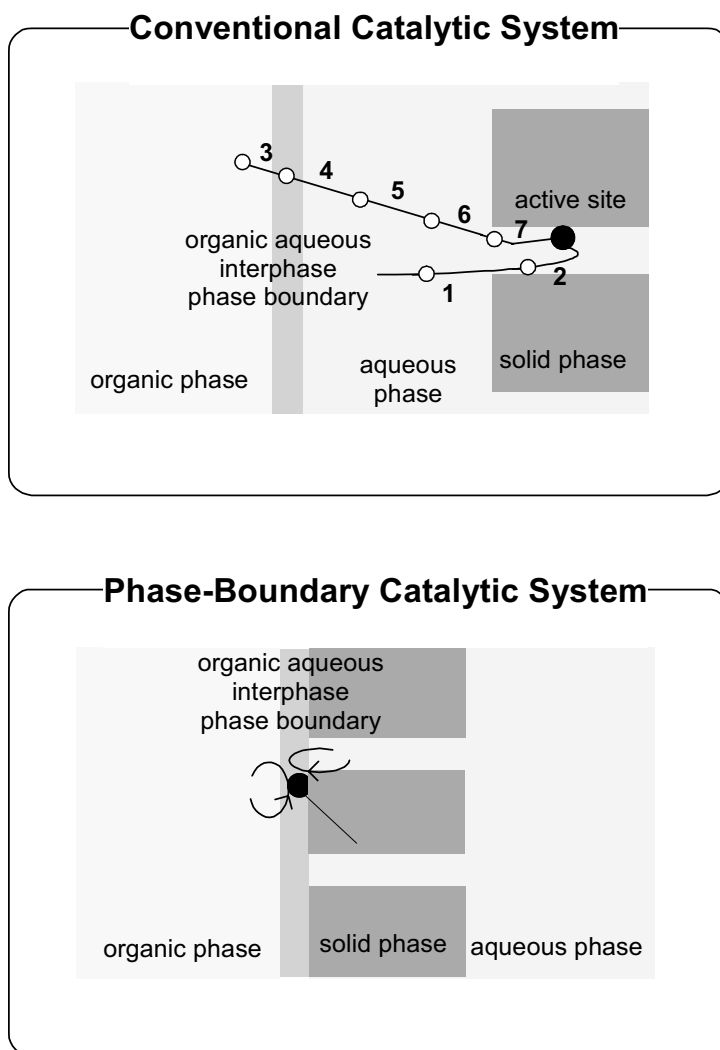


Figure 4: Schematic representation of catalytic action of phase-boundary catalysis in comparison with conventional catalytic system.

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).

It was reported that without vigorous stirring, no reactivity of the catalyst was observed in

conventional catalytic system [25-28]. As proposed in Figure 4, 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 4), 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 [28, 30].

The work in this kind of catalytic system is based on my scientific work in the period of 1999-2002 which was devoted to the development of a novel catalytic system [25-34].

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 [35-38]. 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. Proposed model of bifunctional catalytic system is shown in Figure 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 [39].

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 research was 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.

Photocatalyst

By definition, a photocatalyst is a substance that is able to produce, by absorption of light quanta, chemical transformations of the reaction participants, repeatedly coming with them into the intermediate chemical interactions and

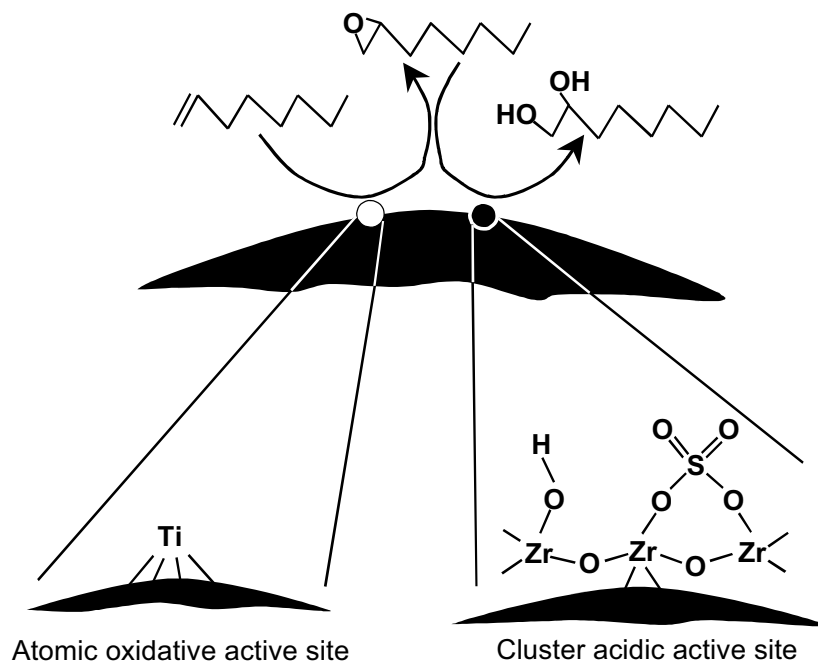


Figure 5: Proposed model of TS-1 loaded with sulfated zirconia as bifunctional catalyst for consecutive transformation of 1-octene to 1,2-octanediol through the formation of 1,2-epoxyoctane [35].

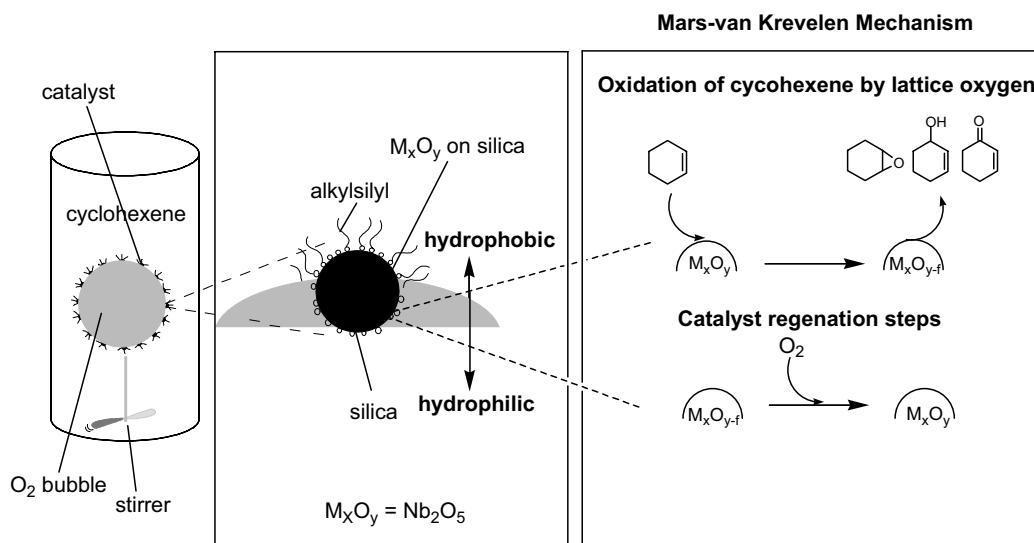


Figure 6: The stabilization of amphiphilic solid particles containing niobium oxide as active sites on liquid-gas (cyclohexene-O₂) for oxidation of cyclohexene with Mars-van Krevelen Mechanism [39].

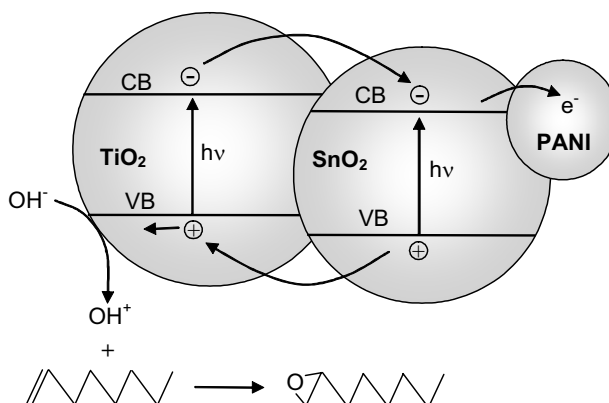
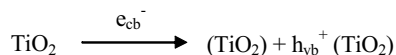


Figure 7: The proposed mechanism of photocatalytic epoxidation of 1-octene over PANI-SnO₂-TiO₂ [41].

regenerating its chemical composition after each cycle of such interactions [40]. Titanium dioxide (TiO₂) is one of the most popular photocatalysts. Photocatalysis over TiO₂ is initiated by the absorption of a photon with energy equal to or greater than the band gap of TiO₂ (3.2 eV), producing electron-hole (e⁻/h⁺) pairs,



Consequently, following irradiation, the TiO₂ particle can act as either an electron donor or

acceptor for molecules in the surrounding media. However, the photoinduced charge separation in bare TiO₂ particles has a very short lifetime because of charge recombination. Therefore, it is important to prevent electron-hole recombination before a designated chemical reaction occurs on the TiO₂ surface. TiO₂ and high recombination rate of the photogenerated electron-hole pairs hinder its further application in industry. Having recognized that charge separation is a major problem, here, SnO₂-TiO₂ coupled semiconductor photocatalyst loaded with PANI, a conducting polymer, has been

studied as photocatalyst in the oxidation of 1-octene with aqueous hydrogen peroxide. We reported that the attachment of polyaniline (PANI) on the surface of SnO₂-TiO₂ composite will reduce the electron-hole recombination during the photocatalytic oxidation of 1-octene due to PANI's electrical conductive properties [41].

Future direction in catalytic science and technology

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 [42]. As formulated by Panel on New Directions in Catalytic Science and Technology, National Research Council, the National Academy of Sciences, USA [43], the future direction in the field of catalysis were in the following areas,

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.

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