Heterogeneous Chemocatalysis: Catalysis by Chemical Design - A Personal Experience

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This author started his research activity on heterogeneous catalysis in 1995 as a Ph.D. student at Universiti Teknologi Malaysia. He 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 of experimental work, the author failed to synthesize VPI-5. Everything in the author’s Ph.D. thesis comes from the last twelve months in the laboratory. Nonetheless, since the author had another project on synthesis of zeolite from rice husk ash that both worked at once, he ended up with three international publications together on the study of the structure, physicochemical properties and catalytic activity of metal-substituted AlPO₄-5. This author also proposed and successful in synthesizing NaA zeolite directly from rice husk and carbonaceous rice husk ash. He finally found out what independently doing good science. It was an exhilarating period. The author finished his Ph.D. project in two and half years in 1998. The author continued work as a postdoctoral fellow for one year at Universiti Teknologi Malaysia. In 1999, the author was fortunate enough to land a postdoctoral position at Catalysis Research Center, Hokkaido University, Japan. 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 half year, the author published a seminal paper on a new concept in heterogeneous catalysis termed “Phase-boundary catalysis”. During stay in Japan, the author learns how to do science right. In May 2002, for one year, the author joined the Ibnusina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia as research officer and in 2003 he accepted his first academic position as lecturer at this university. In this review, an attempt will be made to classify several heterogeneous catalytic systems which contain examples from the author’s experience in this research area. The author’s scientific research in heterogeneous catalysis has been classified into five classes: single center catalyst, hydrophobic-hydrophilic catalytic system, bifunctional catalyst, synergetic multi reaction center catalyst and photocatalyst. The catalysts have been designed for synthesis of useful organic compounds. For detailed information on the research projects and for acquiring some knowledge on research in the covered fields the reader is referred to the pertinent recent publications and references therein.

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I. 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 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.

Table 1: Homogeneous versus heterogeneous catalysis.

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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. 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.

![Figure 1: Schematic representation of the catalyst development cycle.](image)

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.

II. 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. 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.

III. 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 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].

IV. 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 section, a new hydrophobic-hydrophic 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 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].
V. 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.

![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].](image)

VI. 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. 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.

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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.

![Figure 6: 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 [39].](image)

VII. 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 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,

\[
\text{TiO}_2 + \text{h}_b^+ \rightarrow (\text{TiO}_2) + \text{e}_b^-
\]

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].
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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REFERENCES

Hadi Nur was born on 6 May 1969. He specialises in advanced materials and heterogeneous catalysis, typically working on heterogeneous catalyst and catalysis. He received his undergraduate and graduate education in chemistry and materials engineering at Institut Teknologi Bandung, as he received the B.S. degree in 1992 and M.Eng. degree in 1995. Shortly after that, he continued his postgraduate studies in zeolite chemistry at Universiti Teknologi Malaysia (UTM), and received the Ph.D. degree in 1998. His 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, Universiti Teknologi Malaysia. Currently, he is a Senior Lecturer at Ibnu Sina Institute for Fundamental Science Studies. He has supervised many postgraduate students studying for Ph.D. and M.S. degrees in heterogeneous catalysis and advanced materials, for example, zeolite chemistry and catalysis, photocatalysis, semiconductor nanoparticle-polymer composite, bifunctional oxidative and acidic catalysts, and phase-boundary catalysis.