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Some Aspects of Particuology in Heterogeneous Catalysts

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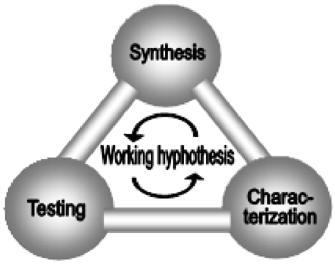
Graphical abstract



Abstract

The design and synthesis of particulate materials for new catalyst systems with novel properties remain a big challenge today. Here an attempt has been made to synthesize particulate materials for several heterogeneous catalytic systems, which contain examples from our recent research projects in this area. The particulate catalysts have been designed for single centre catalyst, phase-boundary catalyst, bifunctional catalyst, photocatalyst and chiral catalyst. In our current research, the synthesis of well-aligned titanium dioxide catalyst with very high length to the diameter ratio has also been demonstrated for the first time by sol-gel method under magnetic field with surfactant as the structure aligning agent.

Keywords: Particulate materials; heterogeneous catalytic system; synthesis of titanium dioxide under magnetic field; liquid-gas boundary catalyst; bifunctional catalyst; photocatalyst; chiral catalyst

Abstrak

Reka bentuk dan sintesis bahan zarah untuk sistem mangkin yang baru dengan sifat novel masih merupakan satu cabaran pada masa kini. Satu percubaan telah dilakukan di sini untuk menghasilkan bahan zarah untuk beberapa sistem pemangkinan heterogen yang mengandungi contoh-contoh daripada projek penyelidikan kami dalam bidang ini. Mangkin zarah ini telah direkabentuk untuk mangkin pusat tunggal, mangkin fasa sempadan, mangkin dwifungsian, fotomangkin dan mangkin kiral. Dalam penyelidikan semasa kami, penghasilan mangkin titanium dioksida dengan susunan sejajar yang kemas dan mempunyai nisbah panjang kepada diameter yang tinggi telah dilakukan dengan pertama kali dengan kaedah sol-gel di bawah medan magnet dengan surfaktan sebagai agen jajaran struktur.

Kata kunci: Bahan zarah; sistem pemangkin heterogen; penghasilan titanium dioksida di bawah medan magnet; mangkin sempadan cecair-gas; mangkin dwifungsian; fotomangkin; mangkin kiral

■1.0 INTRODUCTION

1.1 Particuology in Heterogeneous Catalysis

The term "particuology" was coined to parallel the technical terminologies for the science and technology of particles by combining the Latin prefix particula for particles and the Greek suffix logia denoting subject of study [1]. Particuology in heterogeneous catalysis is an important topic in both of academic and industry point of view since heterogeneous catalysis is one of the most important field in chemical industries. Heterogeneous catalysis is also one of the keys factor for sustainable development of industrial society.

The following are examples of researches that have been carried out in our group. Some of the review on our researches had been published in books and journals [2–4]. This paper also summarizes some of the research that is being conducted in our laboratory at Universiti Teknologi Malaysia. These researches can hopefully serves as an inspiration for readers on 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 further searches for novel approaches to catalysis.

"Catalysis by chemical design" has been a dream for decades. To specify the composition and structure of matter to affect 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 past decades, the promise was perceived as 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 have shown promise, not just for identifying catalytic intermediates and reaction pathways accessible to experiments, but also for providing quantitative predictions of energetic for elementary reaction processes that are not easily accessed experimentally. Much of our work is aimed at the rational design of catalysts for oxidation and acid organic reactions. This branch of chemistry remains one of the most challenging problems in heterogeneous catalysis.

1.2 Better Catalyst through Chemical Design

Catalysts operate at a molecular level. Due to that the study of their mechanisms falls into the realm of nanotechnology: the science of the extremely small particles. Most catalytic chemical reactions are heterogeneous – they involve more than one phase. Usually a gas and/or liquid phase passes through 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.

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.

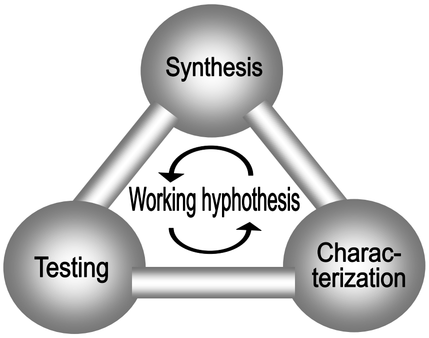


Figure 1 Schematic representation of the catalyst development cycle

■2.0 OUR RECENT RESEARCHES

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. The most basic mechanistic features are well understood. Here, an attempt will be made to introduce several approaches to synthesize particulate catalysts.

2.1 Magnetic Field in the Synthesis of Solid Catalyst

For many years, scientists developed several methods for structural control of organized molecular assemblies, such as the use of a flow and an electric field. Magnetic field is also one of the potential methods to align and orient molecules and domains, because it has an advantage that any materials, even diamagnetic materials can be aligned by magnetic fields, as long as they have magnetic anisotropy. It is well established that diamagnetic assemblies with magnetic anisotropy will be oriented and rotated in a magnetic field to achieve the minimum-energy state. The protocols for producing oriented ordered inorganic-surfactant was reported but only based on simulation theory. The use of TiO_2 as the inorganic precursor and organic surfactant, however, has not been reported. In our recent report [5], well-aligned titanium dioxide was successfully synthesized by sol-gel method by using tetra-n-butyl orthotitanate (TBOT) as the titanium dioxide precursor. Well-aligned titanium dioxide with very high length to diameter ratio synthesized under magnetic field was demonstrated for the first time by sol-gel method under magnetic field (up to 9.4 T) with cetyltrimethylammonium bromide as the structure aligning agent.

Figure 2 shows the scanning electron microscope (SEM) images of TiO_2 samples prepared with various parameters under magnetic field. Without the presence of CTAB surfactant and magnetic field, TiO_2 in block shape (Figure 2a) was obtained. On the other hand, the small granular particles of TiO_2 with sizes of 5 – 15 µm were observed in the presence of CTAB (Figure 2b). Apparently, the results proved that the surfactant played a crucial role in forming granular shaped TiO_2 particles. Under low magnetic field of 2.5×10^{-4} Tesla and with the presence of CTAB, a small fraction of well-aligned TiO_2 was obtained (Figure 2c) in a relatively fast hydrolysis rate of four days, indicating the alignment of TiO_2 was influenced by magnetic field. Interestingly, abundance of well-aligned TiO_2 with the length of 500 – 2000 µm were successfully produced (Figure 2d) with a relatively slow hydrolysis rate of seven days under the same magnetic-field strength. This evidence implied that a slow hydrolysis rate was very important in providing enough time for the formation of abundance of well-aligned TiO_2. Interestingly, the well-aligned TiO_2 was vividly straighter and more compact (Figure 2e) under strong magnetic field of 9.4 Tesla. Without CTAB and with slow hydrolysis (7 days) under strong magnetic field (9.4 Tesla), TiO_2 in block shape (Figure 2f) was obtained. Therefore, we conclude that the use of CTAB surfactant as the structure aligning agent, with slow hydrolysis rate and strong magnetic field are the key factors to well-aligned TiO_2.

2.1.2 A New Way to Control the Coordination of Titanium(IV) in Silica-Titania Catalyst

In another one of our recent researches, a new way to control the coordination of titanium(IV) in the sol-gel synthesis of broom fibers-like mesoporous alkyl silica-titania catalyst through the addition of water has been demonstrated [6]. The tetrahedral and octahedral coordination of Ti(IV) in alkyl silica-titania has been successfully controlled by the addition of water in the sol-gel process. Octadecyltrichlorosilane (OTS) and tetraethyl orthotitanate (TEOT) were used as the precursors. The effect of water addition on the local coordination of Ti(IV) was analyzed by using Fourier transform infrared (FTIR) spectrometer, diffuse reflectance ultra-violet visible (DR UV-Vis) spectrometer, field emission scanning electron microscope (FESEM), X-ray diffraction (XRD) spectrometer and transmission electron microscope (TEM). It was demonstrated that water facilitated the formation of Si–O–Ti bonding, which is related to tetrahedral Ti(IV). These materials exhibit the peak at small angle of X-ray diffractogram and type IV shaped adsorption-desorption isotherms characteristic of mesoporous silica-titania. The mesoporous structure shaped like 'broom fibers', arranged by lamellar like fibers with diameter size of about 3 – 5 nm, has been clearly observed by TEM. The catalytic activity of alkyl silica-titania catalysts obtained was tested in the polymerization of styrene in the presence of aqueous hydrogen peroxide. It showed that the presence of tetrahedral Ti(IV) gave beneficial effects in increasing the activity in this catalytic reaction. Figure 3 shows the TEM image of mesoporous structure shaped like ‘broom fibers’ silica-titania particles.

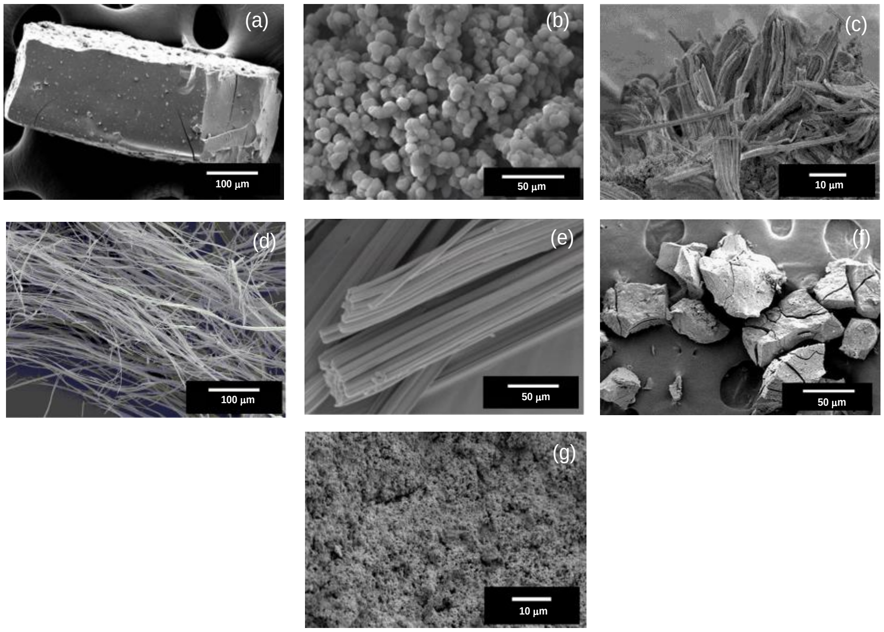


Figure 2 SEM images for TiO_2 samples synthesized with various parameters: (a) without CTAB, with fast hydrolysis (4 days) and without magnetic field, (b) with CTAB, with fast hydrolysis (4 days) and without magnetic field, (c) with CTAB, with fast hydrolysis (4 days) and under low magnetic field (2.5 x 10^{-4} Tesla), (d) with CTAB, with slow hydrolysis (7 days) and under low magnetic field (2.5 x 10^{-4} Tesla), (e) with CTAB, with slow hydrolysis (7 days) and under strong magnetic field (9.4 Tesla), (f) without surfactant, with slow hydrolysis (7 days) and under strong magnetic field (9.4 Tesla) and (g) sample in Figure 2e after calcination at 500°C for 2 h

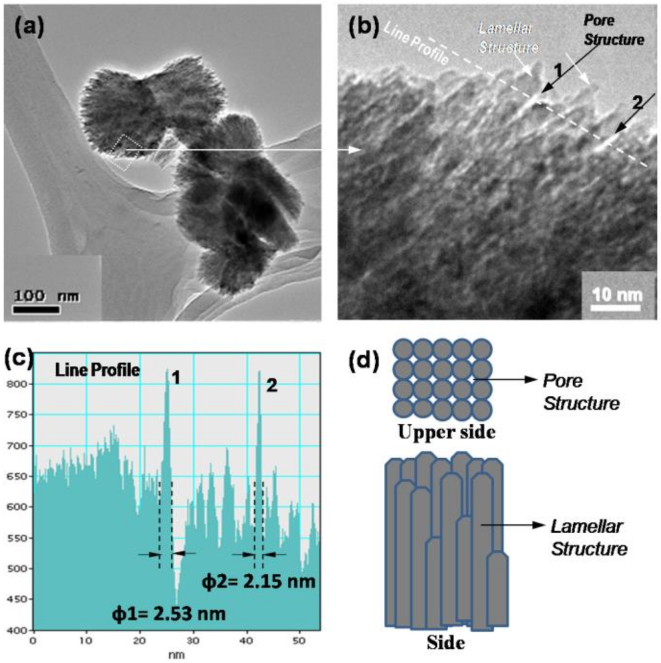


Figure 3 The image, line profile, pore sizes and structure analysis of alkyl silica-titania. (a) TEM image of the alkyl silica-titania material synthesized by sol-gel method at room temperature. (b) TEM image enlarged from the discontinue-lined white square marked area in (a). (c) Line profile of the discontinue-white line in (b). (d) Schematic illustration of the pore formed between the lamellar structured materials

2.2 Liquid-gas Phase-boundary Catalytic System

Synthesis of a solid catalyst that is located in the boundary of immiscible liquid-liquid and liquid-gas systems remain a big challenge today. Previously, we reported the preparation of heterogeneous catalysts in the liquid-liquid phase boundary [7-18]. In this catalytic reaction system, the catalyst was placed at the liquid-liquid phase boundary between aqueous hydrogen peroxide and water-immiscible organic phases and act as an efficient catalyst for epoxidation reaction. In this paper, the study is extended to liquid-gas catalytic system. 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.

The fast-growing insight into the functional materials has led research to be more focused on the synthesis of materials with specific properties. The preparation of hollow materials with low density is one of the targets. Along this line, we have attempted to make an effective heterogeneous catalytic system for this application by using gold/polystyrene-coated hollow titania as the catalyst [19]. Figure 4 shows the schematic illustration of the procedures used for the synthesis of floating gold/polystyrene-coated hollow titania. The catalyst was prepared in several stages; (1) preparation of the template hydrothermally by using sucrose as a precursor, (2) synthesis of hollow titania by using sol-gel method and the removal the carbon template by calcination, (3) polystyrene coating of hollow titania particles and (4) gold sputtering of polystyrene-coated hollow titania.

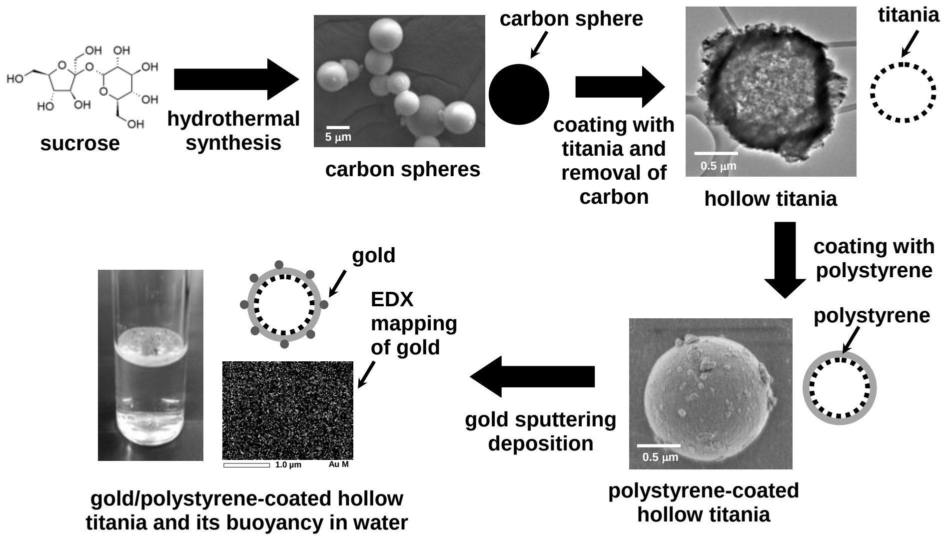


Figure 4 Schematic illustration of floating gold/PS-HT synthesis procedures with TEM image of hollow titania, FESEM images of CS and PS-HT [19]

Reaction between two immiscible liquids will require stirring to maximize the contact area of the reactants. Nevertheless, the reaction between gas and liquid phases also need stirring to increase the solubility of gas into the liquid. Hence, this research will be great if it can utilize floating gold/polystyrene-coated hollow titania catalysts with controllable void and floating properties. Besides that, efficient control of the structural properties of hollow titania themselves and fabrication of gold/polystyrene composites are the other important subject for their application, especially in the field of catalysis. For floating purpose, it is necessary to fabricate polystyrene-coated hollow titania with low density.

2.2.1 Improvement of Catalytic Activity in Styrene Oxidation of Carbon-coated Titania by Formation of Porous Carbon Layer

Here, we demonstrated an approach to improve the catalytic function of titania particle by covering it with porous carbon [20]. Porous carbon layer was formed by treating the carbon-coated titania (C@TiO_2) with KOH solution. Carbon-coated titania (C@TiO_2) was obtained by pyrolysis of polystyrene-coated titania (PS@TiO_2), which was produced by in-situ polymerization of styrene by using aqueous hydrogen peroxide. The presence of polystyrene and carbon on the surface of titania was confirmed by FTIR and XPS. The carbon content was about 2.2 wt% with thickness of carbon layer of ca. 5 nm. After treating with KOH solution, PC@TiO_2 with the pore size of ca. 5 nm, total pore volume of 0.05 cm^2 g^{-1} and BET specific surface area of 46 m^2 g^{-1} was obtained. The catalytic activity results showed that PC@TiO_2 gave a higher activity in styrene oxidation compared to bare TiO_2 and C@TiO_2. The highest catalytic activity was obtained by using PC@TiO_2 that was obtained after treating C@TiO_2 with 1.0 M KOH solution with benzaldehyde and phenylacetaldehyde as the main reaction's products. At higher concentration of KOH solution, the catalytic activity decreased when the crystallinity of TiO_2 decreased. Figure 5 shows the schematic diagram of the preparation of PS@TiO_2, C@TiO_2 and PC@TiO_2 particles and their FESEM and TEM images.

2.3 Bifunctional Catalyst

Another type of catalytic system can be defined as bifunctional. The prototype catalytic system is TS-1 loaded with sulfated zirconia as bifunctional oxidative and acidic catalyst for the transformation of 1-octene to 1,2-octanediol [21-28]. The catalyst concern contains two types of reactive centers, oxidative and acidic. Titanium acts as the active site for the transformation of 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 is consumed in 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 6.

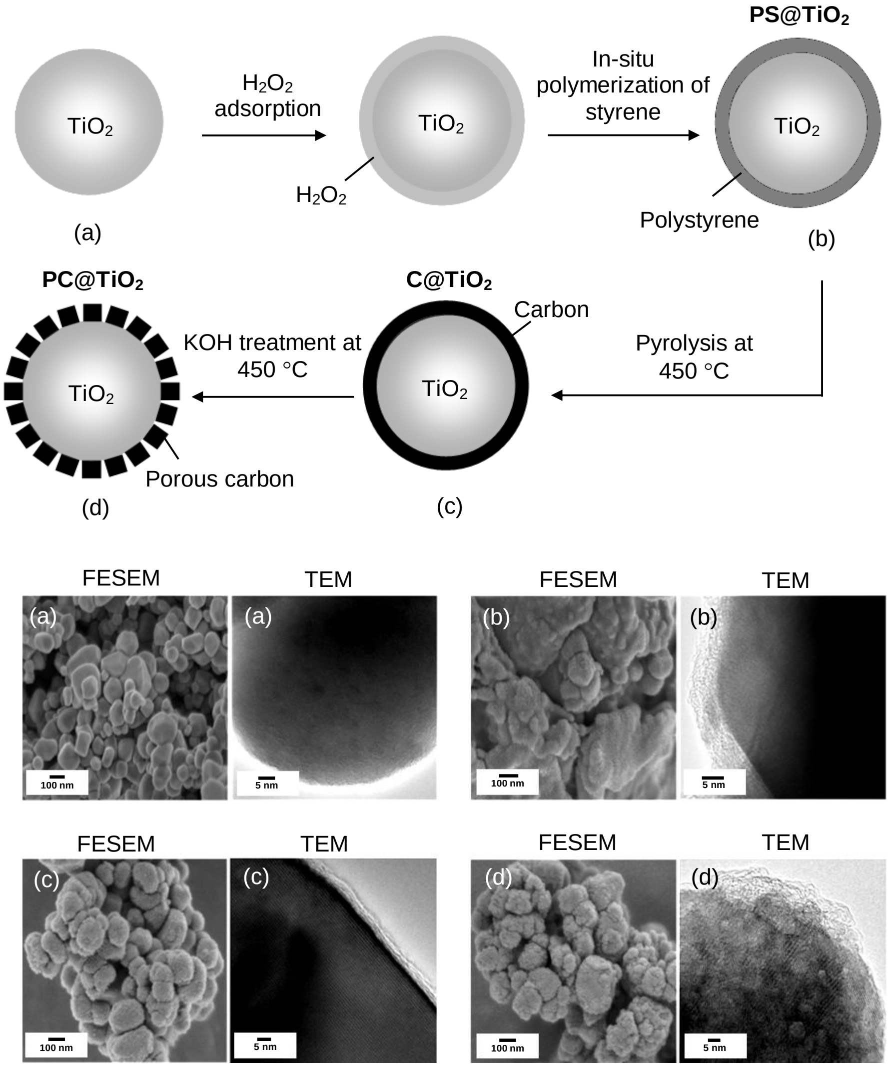


Figure 5 Schematic diagram of the preparation of PS@TiO_2, C@TiO_2 and PC@TiO_2 particles and their FESEM and TEM images [20]

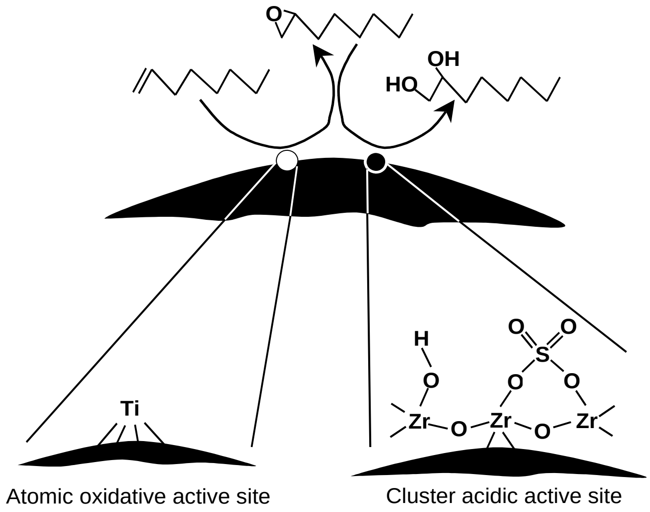


Figure 6 Proposed model of TS-1 loaded with sulfated zirconia as bifunctional catalyst for consecutive transformation of 1-octene to 1,2-octanediol through the formation of 1,2-epoxyoctane [24]

2.4 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 [29]. Titanium dioxide (TiO_2) is one of the most popular photocatalysts. Photocatalysis over TiO_2 is initiated by the absorption of a photon with energy equal to or greater than the band gap of TiO_2 (3.2 eV), producing electron-hole (e^-/h^+) pairs,

$$TiO_2 \xrightarrow{e_{cb}^-} (TiO_2) + h_{vb}^+\,(TiO_2)$$

Consequently, with irradiation, TiO_2 particle can act as either an electron donor or acceptor for molecules in the surrounding media. However, the photoinduced charge separation in bare TiO_2 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 TiO_2's surface. TiO_2 has high recombination rate of the photogenerated electron-hole pairs, which hinders its further application in industry. Having recognized that charge separation is a major problem, here, SnO_2-TiO_2 coupled semiconductor photocatalyst loaded with polyaniline (PANI), a conducting polymer, has been studied as the photocatalyst in the oxidation of 1-octene with aqueous hydrogen peroxide. We reported that the attachment of PANI on the surface of SnO_2-TiO_2 composite will reduce the rate of electron-hole recombination during the photocatalytic oxidation of 1-octene due to PANI´s electrical conductive properties (see Figure 7) [29].

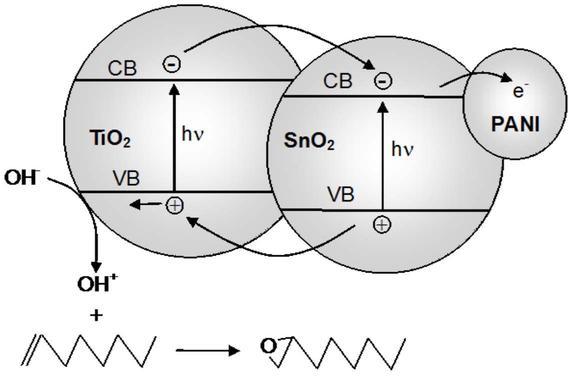


Figure 7 The proposed mechanism of photocatalytic epoxidation of 1-octene over PANI-SnO_2-TiO_2 [29]

2.5 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 the synergistic role of Lewis and Brönsted acidities in Friedel-Crafts alkylation of resorcinol over gallium-zeolite beta. The role of Lewis and Brönsted acidities in alkylation of resorcinol is demonstrated through the gallium-zeolite beta by varying the amount of Lewis and Brönsted acid sites (see Figure 8). The synergism of Lewis and Brönsted acid sites takes place heterogeneously in Friedel-Crafts alkylation of resorcinol with methyl tert-butyl ether to produce 4-tert-butyl resorcinol and 4,6-di-tert-butyl resorcinol as the major and minor products, respectively [30].

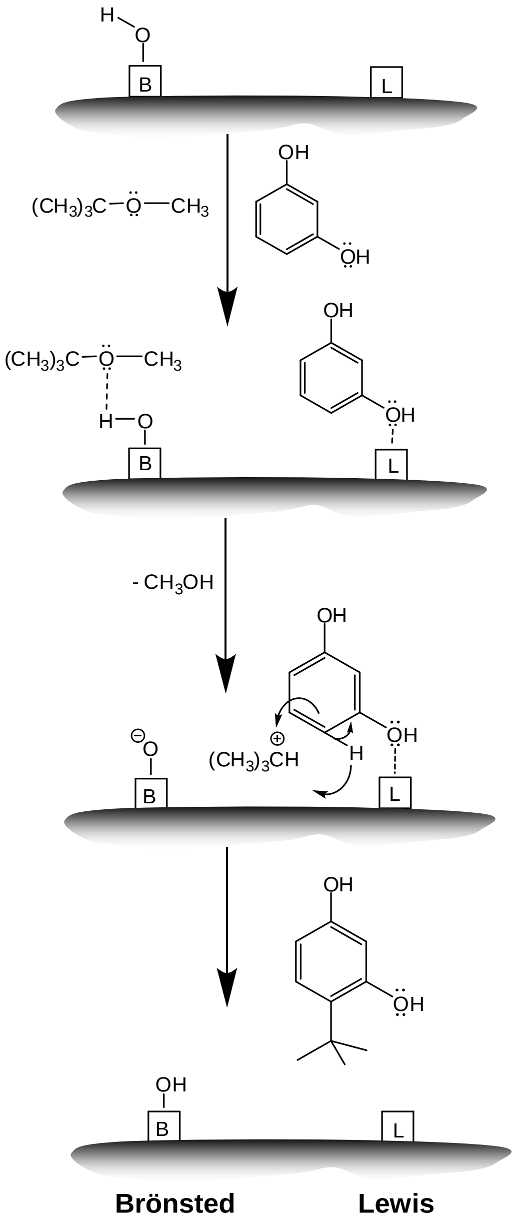


Figure 8 Proposed mechanism of the alkylation of resorcinol with MTBE [30]

2.6 Chiral Catalyst

The control of enantioselectivity by heterogeneous asymmetric catalysis remains a big challenge today. The main drive has been to find new and exciting routes to chiral molecules while achieving high enantiomer selectivity. Here, a new strategy to obtain active catalyst in the enantioselective hydration of epoxyclohexane is proposed [31, 32]. The research strategy is based on the ideas that the enantioselective reactions could be induced by chiral amino acids and the use of heterogeneous catalysis for synthetic purposes will overcome practical separation problems. In order to realize these ideas, chiral amino acid needs to be attached to the hydrophilic part of hydrolyzed octadecyltrichlorosilane (OTS). Amino acids such as L-glutamic acid and L-phenylalanine have been chosen because of their water-soluble properties; hence, they can be easily removed by treatment with water. It is expected that the attachment of amino acid would result in a chiral solid catalyst with bimodal hydrophobic-hydrophilic character. The schematic action of amphiphilic chiral solid catalyst is shown in Figure 9.

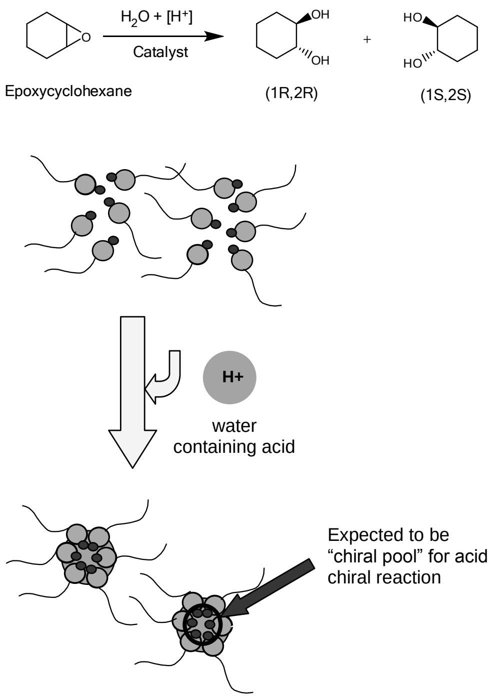


Figure 9 Amphiphilic chiral solid catalyst as heterogeneous micellar catalyst in the enantioselective hydration of epoxyclohexane [31]

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