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PARTICUOLOGY IN HETEROGENEOUS CATALYSIS

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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 was also demonstrated for the first time by sol-gel method under magnetic field with surfactant as 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.

PARTICUOLOGY IN HETEROGENEOUS CATALYSIS

The word "particuology" was coined to parallel the technical terminology 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 the heterogeneous catalysis on of the important field in chemical industries. Heterogeneous catalysisone of the keys factor for sustainable development of industrial society.

The following are examples of my researches,which were carried out by me together with my colleagues and students. Some of there view 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. I hope that these researches can give an inspiration for reader show the design of the catalyst can be related to the physico chemical properties and the catalytic action for the chemical reactions, and may assistin the further search 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 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 have 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.

BETTER CATALYST THROUGH CHEMICAL DESIGN

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.

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.

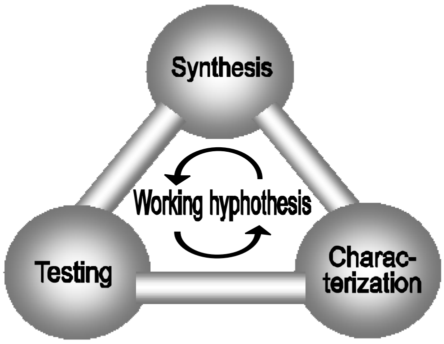

Figure 1. Schematic representation of the catalyst development cycle

OUR RECENT RESEARCHES

A basic feature common to all catalytic systems is that the catalytic reaction can be considered as a reactioncycle, 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 approach to synthesize particulate catalysts.

Magnetic Field In The Synthesis Of Solid Catalyst

For many years, scientists developed several methods for structural control of organized molecular assemblies, such as use of a flow and an electric field. Magnetic field is also one of a potential method 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 the magnetic anisotropy. It is well established that diamagnetic assemblies having magnetic anisotropy will become oriented and rotate in a magnetic field to achieve the minimum-energy state. The protocols for producing orientated ordered inorganic-surfactant was reported but only based on simulation theory. The use of TiO_2 as 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 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 structure aligning agent.

Figure 2 shows the scanning electron microscope (SEM) images of TiO_2samples prepared with vaious 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, results proved that the surfactant played crucial role to form granular shape of TiO_2 particles. Under low magnetic field of 2.5 x 10^{-4} Tesla and with the presence of CTAB, a small fraction of well-aligned TiO_2 was obtained (Figure 2c) in relatively fast hydrolysis rate for 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 relatively slow hydrolysis rate for seven days under same magnetic-field strength. This evidence implied that the 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 closer (Figure 2e) under strong magnetic field of 9.4 Tesla. Without CTAB 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 structure aligning agent, with slow hydrolysis rate and strong magnetic field are the key factors of well-aligned TiO_2.

A New Way To Control The Coordination Of Titanium (IV) In Silica-Titania Catalyst

In our recent research, 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 addition of water[6]. The tetrahedral and octahedral coordination of Ti(IV) in alkyl silica-titania has been successfully controlled by the addition of water in sol-gel process. Octadecyltrichlorosilane (OTS) and tetraethyl orthotitanate (TEOT) were used as precursors. The effect of the addition of water 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 facilitate the formation of Si–O–Ti bond which is related to the tetrahedral Ti(IV). These materials exhibit the pattern of peak at the small angle of X-ray diffractogram and type IV shape adsorption-desorption isotherms characteristic of mesoporous silica-titania. The mesoporous structure shaped like 'broom fibers', arranged by lamellar structure like fibers with diameter size about 3 – 5 nm has been clearly observed by TEM. The catalytic activity of alkyl silica-titania catalysts obtained was tested in polymerization of styrene in the presence of aqueous hydrogen peroxide. It showed that the presence of the tetrahedral Ti(IV) gave a beneficial effect in increasing the activity in this catalytic reaction. Figure 3 shows the TEM image of mesoporous structure shaped like 'broom fibers' silica-titania particle.

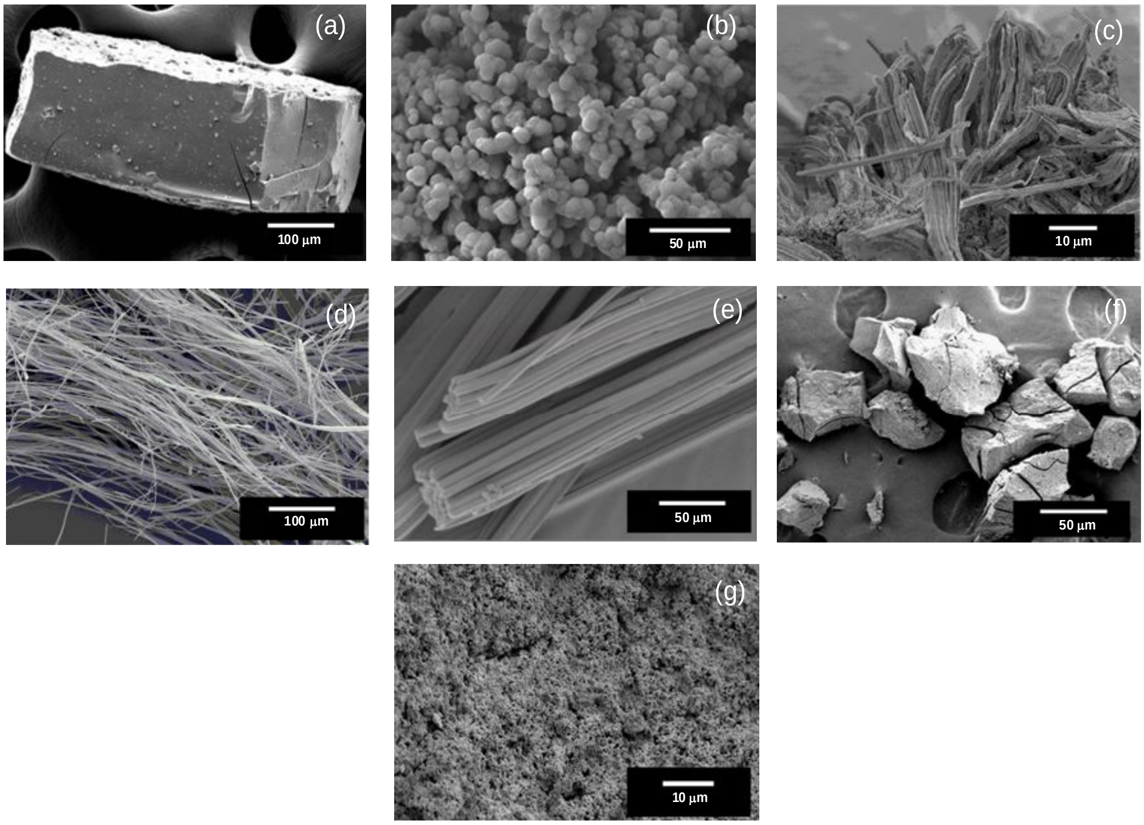

Figure 2 SEM images for TiO_2 samples synthesized with various parameters: (a) without CTAB, with fast hydrolysis (4 days) and without magnetic field, (b) with CTAB, with fast hydrolysis (4 days) and without magnetic field, (c) with CTAB, with fast hydrolysis (4 days) and under low magnetic field (2.5 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.

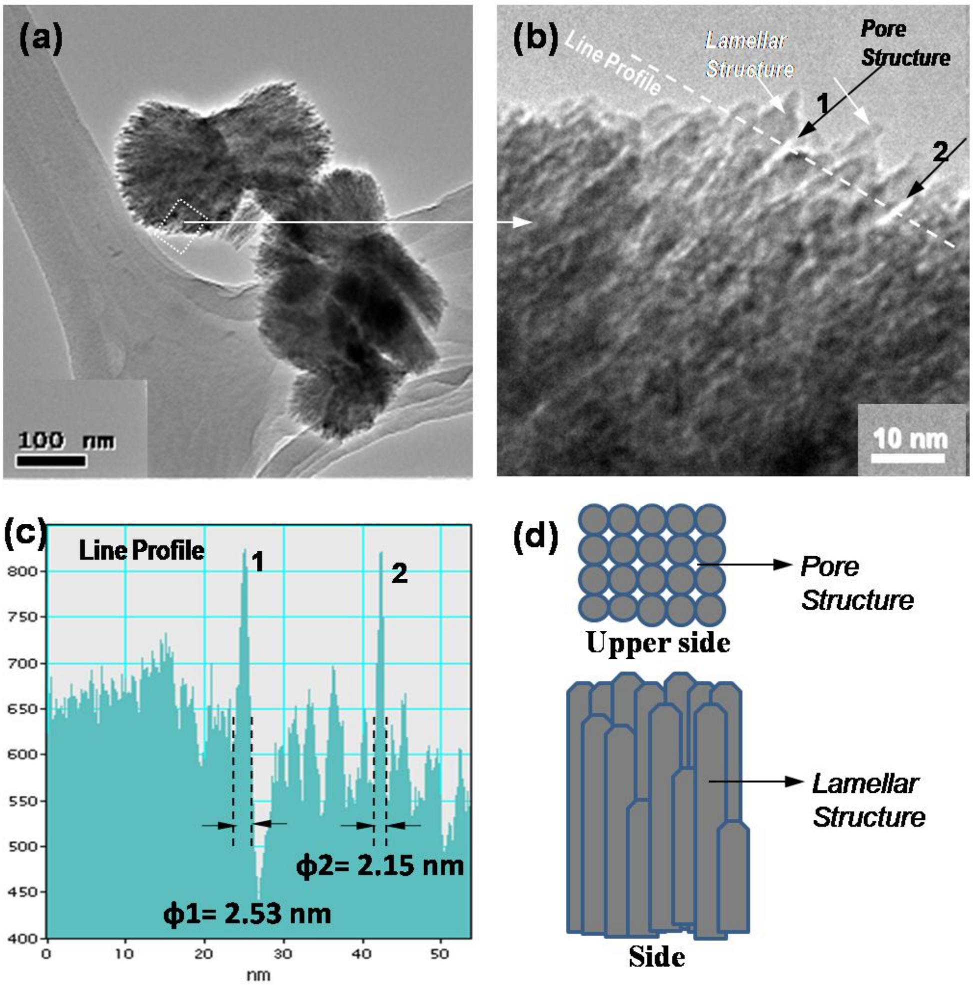

Figure3The image, line profile, pore sizes and structure analysis of alkyl silica-titania. (a) TEM image of the alkyl silica-titania material synthesized by sol-gel method at room temperature. (b) TEM image enlarged from the discontinue-lined white square marked area in (a). (c) Line profile of the discontinue-white line in (b). (d) Schematic illustration of the pore formed between the lamellar structured materials.

Liquid-Gas Phase-Boundary Catalytic System

Synthesis a solid catalyst which can be 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 more focused on the synthesis of materials for the 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 a catalyst[19]. Figure4 shows a schematic illustration of the procedure 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.

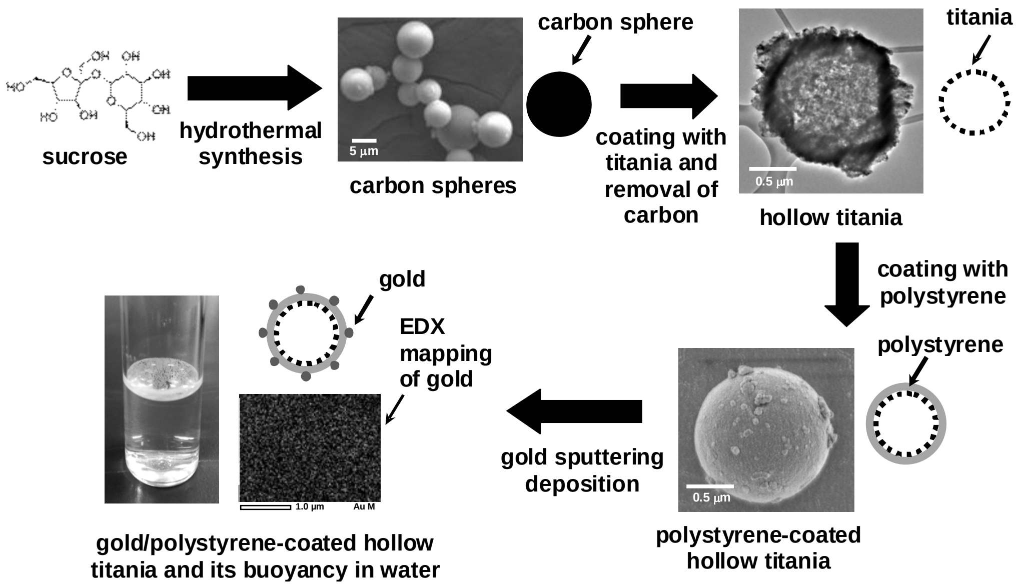

Figure 4. Schematic illustration of floating gold/PS-HT synthesis procedure with TEM micrograph of hollow titania, FESEM micrographs of CS and PS-HT[19]

Reaction between two immiscible liquids will require stirring to maximize the contact area of 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 contribute knowledge in floating gold/polystyrene-coated hollow titania catalysts with controllable void and floating properties. Besides, 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.

Improvement Of Catalytic Activity In Styrene Oxidation Of Carbon-Coated Titania By Formation Of Porous Carbon Layer

Here, we demonstrated that an approach to improve the catalytic function of titania particle by covering it with porous carbon[20]. Porous carbon layer has been 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 were confirmed by FTIR and XPS. Carbon content was about 2.2 wt% with thickness of carbon layer 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^2g^{-1} has been obtained. 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 obtained after treating $C@TiO_2$ with 1.0 M KOH solution with benzaldehyde and phenylacetaldehyde as the main reaction products. At the higher concentration of KOH solution, the catalytic activity decreased when crystallinity of TiO_2 decreased.Figure 5 shows schematic diagram of the preparation of $PS@TiO_2$, $C@TiO_2$ and $PC@TiO_2$ particles and their FESEM and TEM photographs.

Bifunctional Catalyst

Another type 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 transformation of 1-octene to 1,2-octanediol [21-28]. 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 6.

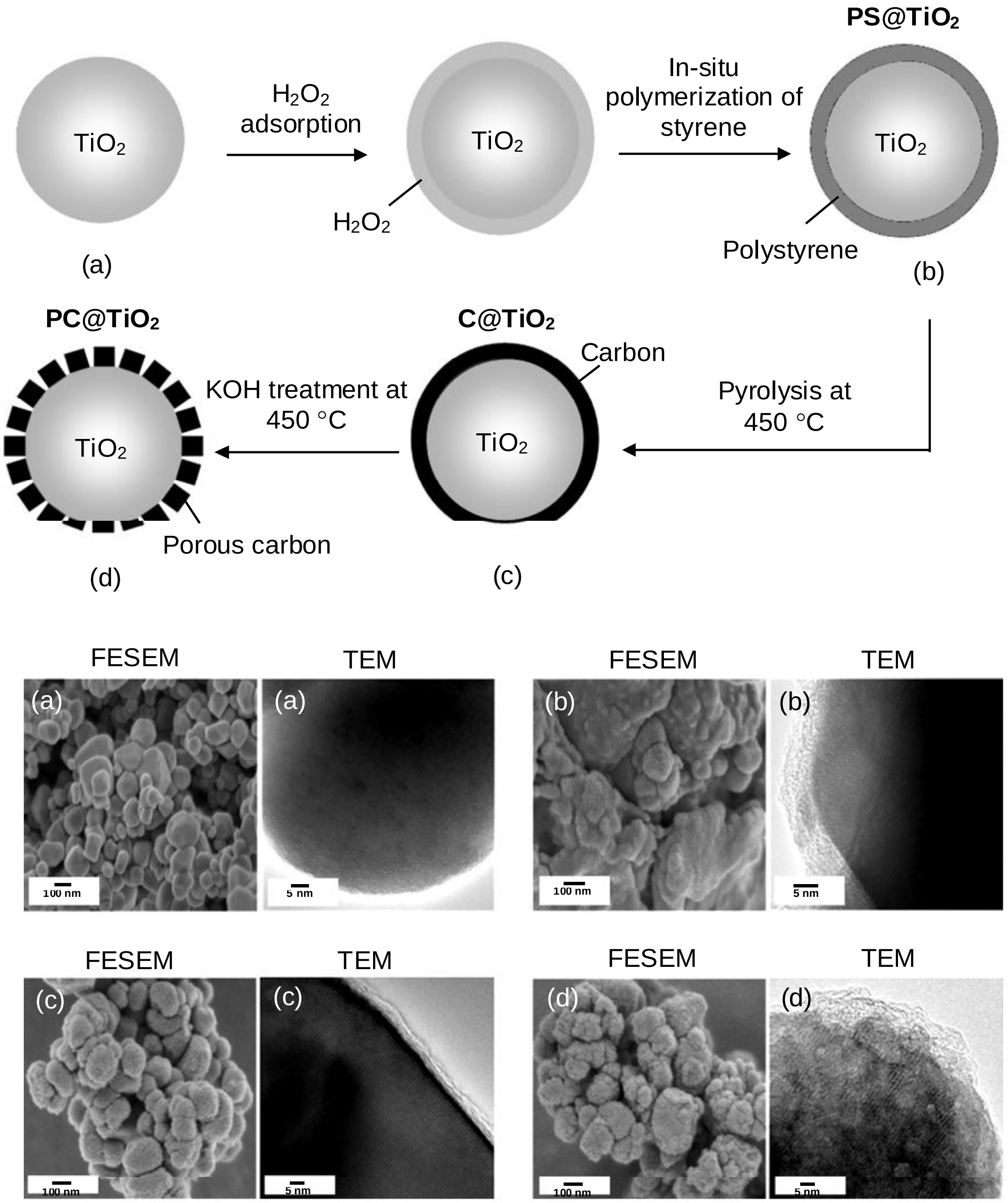

Figure 5. Schematic diagram of the preparation of $PS@TiO_2$, $C@TiO_2$ and $PC@TiO_2$ particles and their FESEM and TEM photographs[20]

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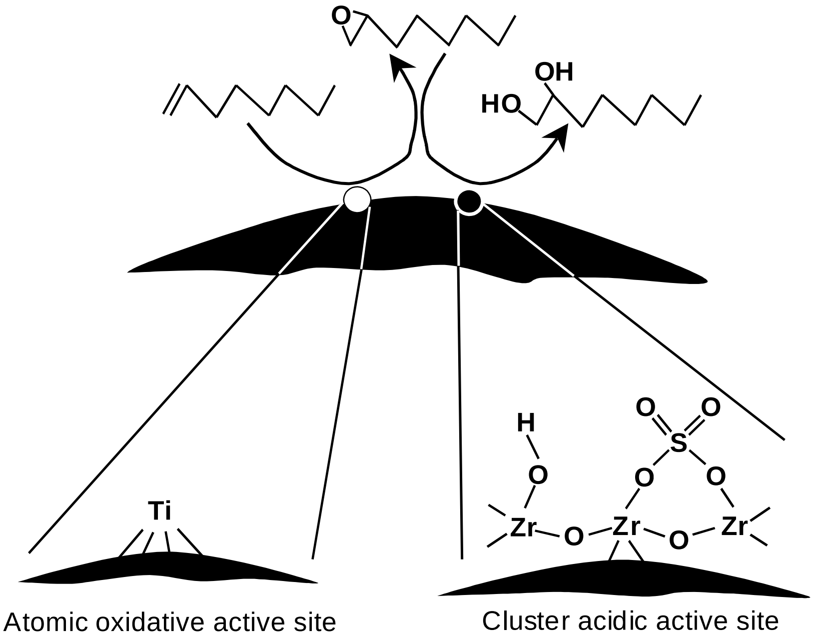

Figure 6. Proposed model of TS-1 loaded with sulfated zirconia as bifunctional catalyst for consecutive transformation of 1-octene to 1,2-octanediol through the formation of 1,2-epoxyoctane[24]

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, following irradiation, the 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_2surface. TiO_2 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, SnO_2-TiO_2 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 SnO_2-TiO_2 composite will reduce the electron-hole recombination during the photocatalytic oxidation of 1-octene due to PANI´s electrical conductive properties (see Figure 7)[29].

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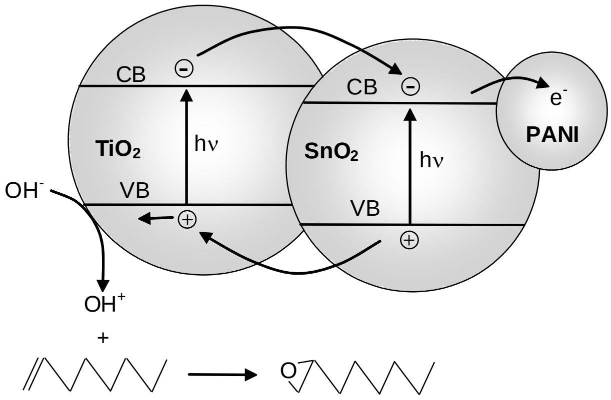

Figure 7. The proposed mechanism of photocatalytic epoxidation of 1-octene over PANI-SnO_2-TiO_2[29]

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 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 take 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].

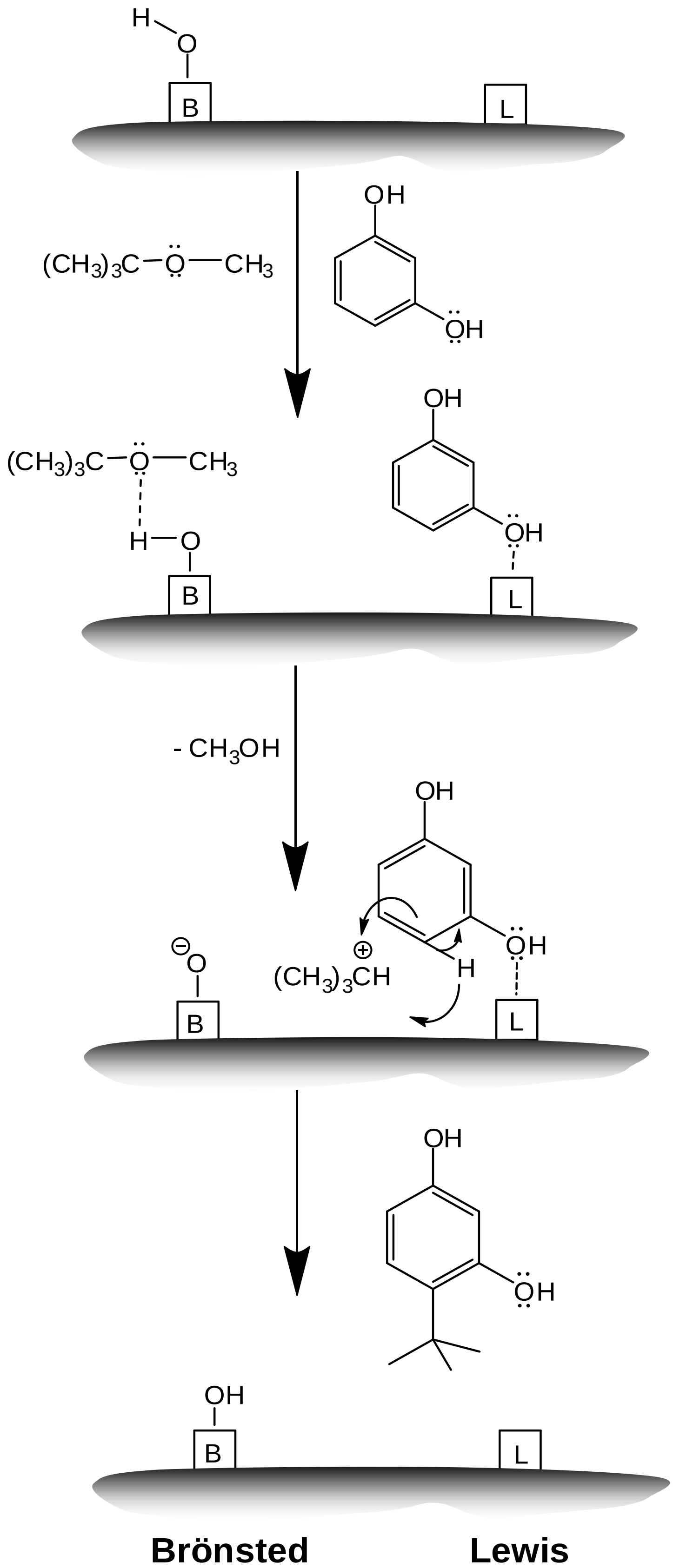

Figure 8. Proposed mechanism of the alkylation of resorcinol with MTBE[30]

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Chiral Catalyst

The control of enantioselectivity by heterogeneous asymmetric catalysis remains a big challenge today. The main drive has been to find new, 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.

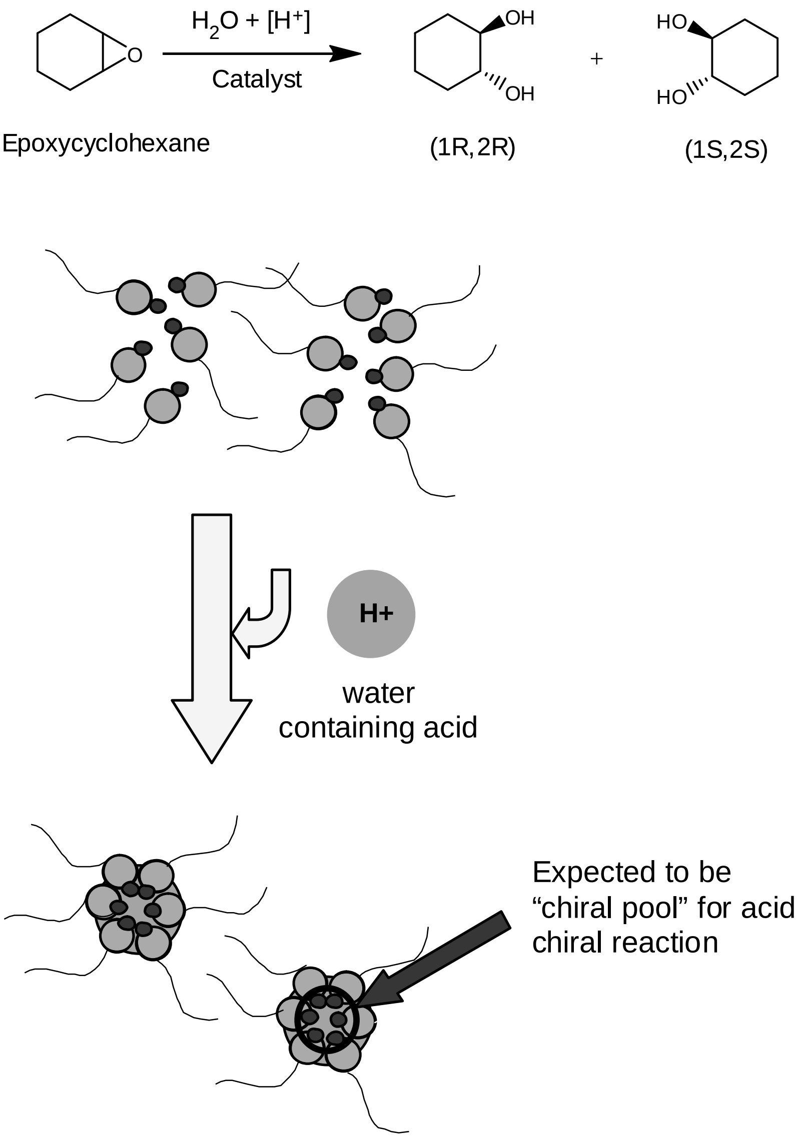

Figure 9 Amphiphilic chiral solid catalyst as heterogeneous micellar catalyst in enantioselective hydration of epoxyclohexane[31]

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