Design of heterogeneous catalysts for selective hydrogenation of cinnamaldehyde and asymmetric hydrogenation of dimethyl itaconate

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2011

Zhen, G. (2011). Design of heterogeneous catalysts for selective hydrogenation of cinnamaldehyde and asymmetric hydrogenation of dimethyl itaconate. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/44557>

<https://doi.org/10.32657/10356/44557>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**DESIGN OF HETEROGENEOUS CATALYSTS FOR
SELECTIVE HYDROGENATION OF
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A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2011

Acknowledgements

It is time to recall the years I spent in Singapore. I feel very lucky, as I have met so many kind people during my PhD study in this foreign place. Here, I try to concentrate all my appreciations into the following sentences.

I would like to thank Professor Yu Du who had helped me a lot when I just started my work in this lab. We together worked on the synthesis of chiral mesoporous materials. This study turns out to be a very important part of this thesis. Without Professor Du's help, my PhD study would not have been finished so soon.

I am grateful to Professor Qinghu Tang and Dr Dapeng Liu for their valuable advices on my research, Dr Shuangquan Hu and Ms. Yuanting Chen for their discussions and supports. I am also heartily thankful to every member of this lab who had helped and encouraged me. They are Mr. Xianyang Quek, Ms. Lusi Li, Mr. Yinchuan Lou, Mr. Munfong Tan, Ms. Shuang Zhou, Ms. Yingshan Tan, Mr. Weizhi Tan, Ms. Nadiah Binte Rahmat and Ms. Beitian Chia.

I would like to thank my families, especially my father for his unprofessional but genuine suggestions about my research and my wife who makes my life in Singapore even more meaningful.

I also would like to thank the School of Chemical and Biomedical Engineering, Nanyang Technological University for the scholarship support.

Finally and most importantly, I would like to express my sincere gratitude to my supervisor, Professor Yanhui Yang, because he always puts my needs prior to his; because he trusts me and allow me to do anything I want to; because he shows me what is a real scientist like. Thanks Yanhui, all the best to you.

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Abstract

As one of the most important industrial processes, catalytic hydrogenation, including both symmetric and asymmetric hydrogenation have found numerous applications in essential areas, such as energy production, agriculture, pharmaceutical, commodity chemicals and environment protection. In general, heterogeneous catalysts are more preferable than homogeneous catalysts due to their recyclability and a wide range of applicable reaction conditions. In addition to the catalytic activity, the selectivity of a hydrogenation catalyst becomes increasingly significant, particularly in fine chemical synthesis industry. In this PhD work, two model hydrogenation reactions—chemo-selective hydrogenation of cinnamaldehyde and asymmetric hydrogenation of dimethyl itaconate were tackled, aiming to find superior heterogeneous hydrogenation catalysts based on the results of many pioneer works. We attempted to contribute new understandings and concepts on the design of hydrogenation catalysts mainly in terms of the strategies of catalyst preparation, physicochemical characteristics of active sites, surface chemistry of supports and specific interactions between the active sites and supports.

In the selective hydrogenation of cinnamaldehyde to cinnamal alcohol, the modifications of electron density and chemical environment of primary catalytic active sites were achieved by forming metallic alloys. Surface islands of metal oxides mainly contributed to the activation of reactant, i.e., cinnamaldehyde in this particular reaction. Moreover, the specific metal-support interaction can be controlled by tuning the surface chemistry of support materials, e.g., oxygen-containing groups. The catalysts were prepared by loading platinum nanoparticles on carbon nanotubes (CNTs)

using a new emerging methodology—microwave-assisted polyol reduction (MAPR). In addition to the conventional characterization techniques, electrochemistry approaches and chemically probed reaction were employed to get insights into the properties of catalysts. Both activity and selectivity were remarkably enhanced by removing the oxygen-containing groups from CNTs surfaces, due to the enhanced electron transfer from CNTs to active sites, increased hydrophobicity of support and suppressed side reactions. Further improvement of catalytic performance was achieved by introducing promoters. Compared to impregnation method, MAPR afforded a close contact between active site and promoter, leading to more efficient electron transfer from promoter to Pt nanoparticle and activation of reactant.

Inspired by the asymmetric hydrogenation over palladium immobilized on a naturally chiral support—silk, we tentatively proposed a conceptual design of chiral catalysts: Pt nanoparticles (presumably no chirality on metallic surfaces) were supported on the synthesized chiral mesoporous silica (CMS) materials. Asymmetric hydrogenation of dimethyl itaconate showed noticeable enantio-bias of products in spite of the fact that the enantio-bias was poor in this particular reaction, which may due to the insufficient chiral inductivity imparted by support surfaces. The chirality of the synthesized CMS materials was evidenced by enantio-selective adsorption and controlled release of chiral drug enantiomers. The formation of local chirality, namely the chirality transfer from chiral templates to the building blocks of CMS materials was investigated using vibrational circular dichroism spectroscopy

To create catalytically active sites with strong chiral discrimination capabilities on the surface of a support material, well-defined homogeneous catalysts composed by

monodentate phosphoramidite ligands (MPL) and rhodium were covalently bonded onto mesoporous silica surfaces. The unique coordination manner of MPL allowed us to control the coordination scheme of immobilized metal complexes by changing the ligand/metal ratio, which was inapplicable in homogeneous system. Interestingly, an opposite enantio-selectivity was observed over the immobilized catalyst, which was tentatively explained by the product adsorption in vicinity of active sites. To improve the low activity and selectivity caused by the varied configuration of ligand and mass transfer resistance, the synthesized homogeneous catalyst was anchored on the CNTs surfaces via π -stacking. The catalytic performances were remarkably preserved in spite of the leaching of active components in the consecutive runs.

Chapter 1 Background and Philosophy

1.1 Background and the driving force for heterogeneous catalysis in selective hydrogenation

In 1835, after reviewing several early studies on chemical reactions, the Swedish chemist Berzelius proposed the existence of a new force—catalytic force which he called catalysis [1]. The concept of catalysis was further verified and developed by many pioneer chemists such as Thénard, Davy, Döbereiner, Ostwald, and Taylor [1, 2]. Nowadays, it is well known that catalysts can dramatically accelerate the reaction rate without changing the equilibrium conditions and being consumed after reactions. Replacement of stoichiometric reactions with catalytic processes allows one to control reaction pathways, shorten reaction time, reduce reactor volume, decrease reaction temperature and minimize waste. Catalytic techniques work in a board range of essential industries including environment, energy, pharmaceutical, agriculture, commodity, electronics and so forth [3-5]. Currently, catalysts have been involved in the manufacture of about 80% of commodities around the globe [3]. As recognition in academia, the Nobel Prizes in Chemistry have been awarded 13 times to laureates who have been working on catalytic chemistry by 2010.

Hydrogenation, as one of the typical catalytic reactions, has diverse applications in petrochemical, pharmaceutical and food industries, as shown in Figure 1.1. In practice, most of hydrogenation processes are conducted in the presence of catalysts. Molecular hydrogen usually serves as the primary hydrogen source for hydrogenation. Nonetheless, some alternative hydrogen sources, such as hydrazine, isopropanol and formic acid, allow reducing the unsaturated organic compounds under mild conditions,

which are called transfer hydrogenations [6]. The earliest example of hydrogenation reaction is the hydrogenation of oxygen over spongy platinum at room temperature, i.e., controlled combustion of hydrogen in oxygen [1]. In the 20th century (the era so called renaissance of catalytic chemistry), the development of catalytic hydrogenation processes has been playing an important role in the evolution of modern industry. Sabatier et al. firstly discovered that hydrogen can be added to carbon compounds catalyzed by metallic catalysts, e.g., hydrogenation of benzene over finely divided nickel metals [7]. The product of benzene hydrogenation cyclohexane is primarily used in adipic acid production, a precursor of nylon [7]. Hydrogenation of arene is also employed to reduce the content of aromatics in diesel fuels, preventing the exhaust of carcinogens from engines [7]. Another important industrial hydrogenation reaction is the hydrogenation of plant oil patented by Normann in 1903 [8]. This particular hydrogenation process provides distinctive flavor, crispness, creaminess and the stability of common food against being oxidized [9].

Figure 1.1 Applications of hydrogenation processes and corresponding examples.

One of the most significant industrialized hydrogenation processes is Haber-Bosch process in which nitrogen is hydrogenated to ammonia. Haber-Bosch process fixes about 98 million ton of nitrogen per year mainly for agricultural purposes [10]. Catalytic hydrogenation is of importance in naphtha reforming that increases the octane number in transportation fuels [9]. In order to satisfy the increasingly stringent restrictions on sulfur content in automobile emission, hydrodesulphurization (HDS, including both hydrogenolysis and hydrogenation steps) becomes a more and more essential catalytic process in the petroleum industry. Almost all the crude oil produced in year 2004 (around 3.9 billion tons) has been treated by HDS processes [9]. The Fischer-Tropsch synthesis may also be deemed as a hydrogenation step, in which carbon monoxide is hydrogenated to liquid fuels [11]. This process has received rapidly growing interests as an approach to produce low-sulfur content diesel fuels [9]. Nowadays, enormous efforts have been devoted to investigate the hydrogenation in transforming biomass to biofuels [12] and value-added fine chemicals [13], driven by the demand for sustainable transportation fuels and “green chemistry”.

In the early stages of catalytic hydrogenation study, stimulated by the tremendous demand on automobile fuels and starting material for commodity chemicals, most of the research efforts focused on improving the activity (i.e., turnover frequency) of catalysts rather than the selectivity [14]. However, the development of fine chemical industries including pharmaceutical, food additive, agrochemical and fragrance becomes increasingly dependent on catalyst with a significantly high selectivity towards a specifically desired product [15], due to the fact that the qualities of products can be largely influenced by impurities and molecular configurations, e.g.,

the properties of isomers from asymmetric hydrogenation may be different or even opposite [4, 16, 17]. On the other hand, minimizing the formation of by-products as a result of highly selective catalytic processes lowers the waste production and energy consumption in the subsequent purification steps, thus selective catalysts are also of environmental significance [14].

In general, selective hydrogenation can be classified into three types as follows (see Figure 1.2 [18]):

Type I selectivity: hydrogenation of mixture of unsaturated compounds, e.g., competitive hydrogenation of toluene and benzene [19].

Type II selectivity: hydrogenation of one starting material involving two or more parallel reaction pathways, leading to different products, e.g., hydrogenation of unsaturated aldehyde [20] and diene [17], as well as asymmetric hydrogenations.

Type III selectivity: hydrogenation of one or several functional groups taking place in a stepwise manner, e.g., hydrogenation of carboxylic acid to the corresponding aldehyde and partial hydrogenation of alkyne to alkene [18].

For a single substrate, there may also be three type of hydrogenation selectivities: chemo-, regio- and stereo-selectivity (see Figure 1.2) [17]. Chemo-selectivity is considered when hydrogenating a compound with more than one kind of unsaturated functional groups, e.g., the hydrogenation of α , β -unsaturated aldehyde. For the substrate with only one kind of unsaturated functional groups presenting at different positions, the issue of regio-selectivity is addressed, e.g., the hydrogenation of diene. Stereo-selectivity is referred to a hydrogenation reaction in which one stereoisomer, enantiomer or diastereomer is more preferably generated compared to others.

Figure 1.2 Types of catalytic selective hydrogenation reactions.

For a long period of time, most of the industry hydrogenation processes (around 75% of the hydrogenation manufactures) and laboratories have been performed under heterogeneous catalytic conditions. Compared to homogeneous catalysts, the advantages of heterogeneous catalysts are overwhelming, such as the ease of recovery, high stability under harsh reaction conditions, re-usage and application in continuous processes. Nonetheless, the mechanistic understanding on hydrogenation steps is usually derived from homogeneous hydrogenating reactions [9]. A well-established example is the homogeneous hydrogenation catalyzed by a metal complex— $\text{Rh(I)Cl(PPh}_3)_3$ (Ph = phenyl), also known as the Wilkinson's catalyst [9]. Inspired by Wilkinson's catalyst, efficient asymmetric hydrogenation catalysts with extremely high enantio-selectivities have been developed during last several decades [21]. Thus, the asymmetric synthesis by hydrogenation is no longer the specialty of nature.

Considering the apparent advantages of both homogeneous and heterogeneous catalysts, heterogenizing a well-defined homogeneous catalyst on a solid surface is always a hot topic in the catalysis community [15, 22].

1.2 Aims and outline of this dissertation

On account of the academic and industrial significance of heterogeneous hydrogenation process, chemo-selective hydrogenation of cinnamaldehyde and stereo-selective (or enantio-selective) hydrogenation of dimethyl itaconate are chosen as model reactions in this Ph.D. study, aiming to understand and rationally design heterogeneous hydrogenation catalysts. In the cinnamaldehyde selective hydrogenation, a relatively new method—microwave assisted polyol reduction (MAPR) is employed to prepare multi-walled carbon nanotubes (CNTs) supported bimetallic catalysts. It is demonstrated that this MAPR method afforded the close contact between promoters and primary Pt active sites, resulting in remarkably enhanced selectivity and activity towards desired unsaturated alcohol. The catalysts were characterized using several conventional characterization techniques, e.g., X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and X-ray diffraction (XRD). In addition, the surface property of support as well as interaction between active center and promoter are unveiled with the aid of electrochemical measurements including CO stripping and cyclic voltammetry (CV). Details of these results are presented in Chapter 4.

Numerous effective heterogeneous chiral catalysts have been developed for asymmetric hydrogenation in such a way that homogeneous chiral catalysts are immobilized on regular (achiral) support surfaces. Inspired by the asymmetric

hydrogenation catalyzed by Pd loaded on a naturally chiral support—silk [23], a conceptual catalyst structure design for asymmetric hydrogenation reaction is tentatively proposed, in which achiral metallic nanoparticles are supported on the surfaces of a novel chiral mesoporous silica (CMS) material, synthesized by using achiral surfactants as templates and a cobalt complex with propeller structure as the co-template. The chirality of CMS was substantiated by enantioselective adsorption and release of drug enantiomers. Based on the characterization results of vibration circular dichroism (VCD) spectroscopy, the chiral discrimination capability of these CMS materials was contributed by the SiO_4 distorted tetrahedron or silica chiral oligomers on the pore wall surfaces. Platinum nanoparticles are loaded on these novel chiral support materials by MAPR, and the preliminary catalytic application in asymmetric hydrogenation of dimethyl itaconate, for the first time, is explored in Chapter 5. The results suggest that the application of an inorganic chiral support material in the asymmetric hydrogenation over achiral metallic nanoparticles as the primary active sites is only a conceptual study due to the weak steric effect that support can exert on the reactants. Aiming to enhance the chirality of these novel chiral support materials, the synthesis is optimized and the formation mechanism of CMS is studied, these results are illustrated in Chapter 6.

In Chapter 7, we attempt to anchor chiral metal complexes on the surfaces of solid supports, which is considered to be a feasible way to prepare heterogeneous hydrogenation catalysts with strong chiral active sites. The synthesis and immobilization of monodentate phosphoramidite ligands (MPL) and their applications in the asymmetric hydrogenation of dimethyl itaconate are carried out. Metal

complexes constituted by MPL are of our interest not only because of their promising applications in asymmetric hydrogenation of substituted olefins [21], but also their unique coordination schemes. Different from conventional bi- or multi-dentate ligands, there is only one atom (phosphorous) in each MPL coordinating with metal cation, thus mixture of different MPL (hetero-complex, see Scheme 1.1a) is possible in the same coordination sphere, which may be a facile methodology to tune the chemistry of active metal center [21]. In addition, some asymmetric hydrogenation results indicated that metal complexes bearing only one MPL (mono-complex, see Scheme 1.1b) also exhibited good activity and selectivity [24, 25]. However, the preparation of mono- and hetero-complexes in a pure form in solution is challenging due to the equilibrium of ligand-metal coordination.

Scheme 1.1 Formation of homo-, hetero- and mono-coordinated complexes in solution (a, b) or on carrier (c)

In this study, the MPL is anchored on the surfaces of rigid solid supports which may promote the formation of either mono- or homo-complexes in a controlled

manner, as shown in Scheme 1.1c. When mesoporous silica—SBA-15 is employed as the support, metal complexes are immobilized via covalent bonds. The results show a good recyclability of synthesized catalysts due to the strong bonding between support surfaces and active sites. However, the low activities of immobilized mono- and homo-complexes are also observed, which is contributed by the mass transfer resistance in SBA-15 mesoporous channels. No enantio-bias is found over mono-complexes immobilized on SBA-15, implying that the chiral discrimination capability of immobilized mono-complexes is insufficient, which may due to the change in molecular structure of immobilized ligand. In contrast to the homogeneous counterpart, an opposite enantio-selection is observed over the immobilized homo-complexes, although the enantio-excess is not pronounced. This unusual phenomenon is tentatively explained by the adsorption of products around the active site, leading to the deviation of catalytic behavior. To overcome the problems encountered in SBA-15, mono- and homo-complexes are also immobilized on CNTs surfaces by π -stacking. Improved activity and selectivity are achieved; nonetheless, the leaching of active components in the reaction is serious due to the weak bonding between active sites and carrier surfaces by π - π interaction.

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Chapter 2 Literature Review

It is no doubt that deep understanding on the mechanism of hydrogenation pathway is of paramount importance for designing hydrogenation catalysts with superior activity and selectivity. Given a catalytic hydrogenation process, catalyst properties can be determined by many influential factors, such as intrinsic nature of catalytic active center, support material, preparation method, reaction parameter and substrate. These guidelines for designing a heterogeneous hydrogenation catalyst will be discussed in the following sections. In addition, advances in selective hydrogenation, asymmetric hydrogenation and synthesis of chiral inorganic materials are also summarized in this chapter.

2.1 General mechanism of hydrogenation pathways

Attributed to the advances in nuclear magnetic resonance (NMR), infrared spectroscopic and kinetic measurements, the mechanism of homogeneous hydrogenation is now well understood, which makes it possible to rationally design an effective catalyst for highly selective hydrogenation [1]. The concept of hydride is vital for elucidating the hydrogenation pathways. The metal complex containing metal-hydrogen bond (M-H) is called hydride in which hydrogen serves as a uninegative monodentate ligand [2]. A hydride, as a crucial hydrogenating intermediate, can be electrically negative, positive or neutral depending on the ligands and overall charge. Most of hydrides are formed by combining metal complexes with molecular hydrogen. This reaction is referred to as di-hydrogen activation which may occur in either homolytic or heterolytic way [2], as shown in Equation (2.1) and (2.2), respectively:

The hemolytic formation of a hydride is an oxidative addition, namely the metal is oxidized. In the heterolytic activation, an intermediate involving a non-classical molecular di-hydrogen species has been proposed [2], therefore, both formal oxidation state and coordination number of the metal center remain unchanged.

Scheme 2.1 Catalytic cycle of alkene hydrogenation over a Wilkinson's catalyst

A typical catalytic hydrogenation cycle in a homogeneous solution usually includes four steps: (1) formation of hydride; (2) coordination of unsaturated substrate; (3) insertion of unsaturated substrate into $\text{M}-\text{H}$ bond; (4) complete hydrogenation of substrate and recovery of catalyst [2]. Take Wilkinson's catalyst as an example, the

primary catalytic cycle of alkene hydrogenation is shown in Scheme 2.1. The rate-determining step is step (3), i.e., the insertion of alkene. The mechanism of catalytic hydrogenation of ketones, aldehydes and imines is similar to that of olefins, the difference is that the heteroatom may coordinate with metal other than the double bond between carbon and heteroatom [2], e.g., hydrogenation of ketone as illustrated in Equation (2.3):

Nevertheless, not all the hydrogenations follow the aforementioned routes. Recently, it has been found that hydrogenation of ketones and imines may be achieved by successive proton transfer from a cationic metal di-hydride and then a neutral metal hydride to the substrate [3]. Isomerization may also take place during the catalytic hydrogenation, which usually leads to undesired products. As shown in Scheme 2.2, when the coordinated alkene is inserted in the M-H bond, the addition of metal and hydrogen may proceed in either Markovnikov or anti-Markovnikov pathway [2]. The direction of addition is influenced by the steric factors and the polarity of M-H bond [2]. The mechanism of hydrogenation over an immobilized homogeneous catalyst is similar to its homogeneous counterpart, while the effect of support has to be considered.

Scheme 2.2 Isomerization of alkene due to the double bond migration.

The generally accepted mechanism for heterogeneous hydrogenation over metal surfaces (Horiuti-Polanyi mechanism) is based on the Langmuir-Hinshelwood model in which both hydrogen and substrate (e.g., alkene) are adsorbed on the catalyst surfaces [4]. The adsorbed hydrogen molecules can dissociate to afford surface hydrides, and the resulting activated hydrogen atoms migrate to the adsorbed alkene substrate to form a surface alkyl-metal complex, followed by the desorption of alkane product from the metal surfaces [4], as shown in Scheme 2.3a. All the steps are reversible except the rate-determining step—leaving of alkane. Isomerization may also take place (see Scheme 2.3b) and the rate of isomerization is inversely proportional to the density of surface hydrides [2]. According to this hydrogenation mechanism, it is appreciable that the activity and selectivity of catalysts may be influenced by the inherence of metal, support and metal-support interaction (which can be modified by preparation strategies).

Scheme 2.3 (a) Heterogeneous hydrogenation of alkene; (b) Isomerization of alkene over a heterogeneous catalyst.

2.2 Catalytic active centers of heterogeneous hydrogenation catalysts

Transition metals, in form of metals, alloys, oxides or sulfides, have been widely employed as catalytically active components for heterogeneous hydrogenation [5]. Homogeneous transition metal complexes are also heterogenized by anchoring on a proper support material surface such as silica [6] and polymer [7]. In general, different metals or metal at different states (e.g., oxide and sulfide) have distinct hydrogenation capabilities. It has been recognized that platinum and palladium can promote the bonding of hydrogen and oxygen at room temperature, whereas cobalt and nickel may only act catalytically in hydrogenation at an elevated temperature [8]. The difference in hydrogenation activities of catalysts has been explained based on their valences, unshared electrons, atomic radii and states of hydrides, etc. [9]. The selectivity and side reactions are also determined by the choice of elements. For example, the metals in the second-row in the periodic table (group VIII Ru, Rh, Pd) lead to substantial isomerization in hydrogenation of olefins, whereas the third-row metals (group VIII Os, Ir, Pt) give rise remarkably low isomerization activities [5]. Although most transition metals exhibit excellent catalytic properties at metallic states, their oxide and sulfide compounds also show reasonable activities in some hydrogenation reactions, such as the hydrogenation of carbon monoxide to methanol catalyzed by zinc oxide [10]. Hydrogenation reactions catalyzed by metal sulfides usually perform under a condition of high temperature and pressure, nonetheless, metal sulfides are resistant to poisons, enabling them feasible to hydrogenate substrates with impurities [5].

Usually, finely dispersed nano-sized active components are preferred due to the high activity as a result of large specific surface areas, e.g., sponge-like Raney Nickel [2]. However, high activity is usually accompanied by a poor selectivity, especially when the reaction is structure sensitive according to Boudart's classification [11]. Small metallic particles possess more diversified crystal planes compared to large particles, and different facets of a given metal cluster may lead to different products, a typical example is the selective hydrogenation of α , β -unsaturated aldehyde over platinum nanoparticles [12]. In recent years, hydrogenation over bimetallic catalysts has also been a hot research area. The second metal either in oxide state or mixed with main active metal forming an alloy may affect the hydrogenation behavior due to the synergistic interaction between promoter (the second metal) and primary active center [13]. For the immobilized metal complex catalysts, the chemistry of catalytic center can be carefully tuned by varying the steric and electronic properties of ligands. Therefore, in addition to the selection of metals, ligand design plays a crucial role in determining the activity and selectivity of a particular anchored catalyst. [1].

Catalytically active center plays the role as the heart of a catalyst, failing to appropriately protect catalytic sites may lead to rapid deactivation of catalysts. The deactivation may be caused by many factors, such as sintering of small metallic nanoparticles, deposition of inactive carbon compound (e.g., graphite, active carbon and coke), poisoning by strongly adsorbed impurities (e.g., sulfur compound) or metallic phase transformation of active centers [14]. In liquid-phase catalytic hydrogenation, catalysts may be deactivated by dissociation of ligands, deposition of carbonaceous substances on the active sites, and blockage of the support pores [15].

The deactivation can be overcome by careful control of reaction parameters, modification of catalytic centers and purification of feed stocks [14, 16]. Nevertheless, in some cases, deactivation or aging of catalysts is useful to promote the selectivity towards the desired products because the poor activity not only impedes the deposition of carbonaceous compounds but also results in less formation of by-products [16]. A well-known example is semi-hydrogenating alkyne to alkene over lead poisoned palladium supported on CaCO_3 —the Lindlar catalyst [5].

2.3 Supports of heterogeneous hydrogenation catalysts

In practical aspects, most catalytic active centers are dispersed on supports to form supported catalysts due to their advantages over the unsupported counterparts in hydrogenation [5]. Generally, a higher dispersion of active components enables more economical utilization of metal especially when using noble metals. Moreover, highly dispersed metallic nanoparticles possess a low reduction temperature which facilitates the activation of metal centers [5].

Table 2.1 Structural parameters of common supports for hydrogenation catalysts.

Supports	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
α -Al ₂ O ₃ ^a	0.1-5	--	500-2000
Kieselguhr ^a	2-35	1-5	>100
Activated Al ₂ O ₃ ^a	100-350	0.4	4-9
SiO ₂ -Al ₂ O ₃ ^a	200-600	0.5-0.7	3-15
SiO ₂ ^a	400-800	0.4-0.8	2-8
Zeolite ^a	400-900	0.08-0.2	0.3-0.8
Active carbon ^a	800-1200	0.2-2.0	1-4
Mesoporous silica ^b	>700	>1.0	2-10
Carbon nanotube	100-800 ^c	0.3-1.6 ^c	1-50 ^d

^{a, b, c d} the data are based on reference [5], [17], [18] and [19], respectively.

A support material should be easy to access, inexpensive, and stable during reactions. Some commonly adopted support materials and their structural parameters are listed in Table 1.1. Large specific surface areas and pore volumes can facilitate the loading and dispersion of catalytically active components, large pore size may accelerate the reaction rate by decreasing the internal diffusion resistance [20]. Furthermore, the selection of support may also depend on its specific chemical properties, as the surface chemistry of support may drastically affect the catalytic behavior.

The influence of support on catalytic hydrogenation is dominated by the inherent property and structure of support in terms of support-active site and support-substrate interactions. The metal-support interactions can be weak, medium or strong (usually denoted as WMSI, MMSI and SMSI, respectively) [21]. In WMSI, the interactions between active metal and support are due to the Van der Waals attractions. Metals confined in zeolite cages can be classified as MMSI, whereas SMSI may occur in the case of metals supported on reducible oxides [21]. These interactions affect the catalytic properties by affording the formation of active sites on the metal-support interface or directing (confining) the growth of metal particles [22]. Acid support such as Al_2O_3 is prone to extract electrons from metal particles, which, in turn, leads to the high activity for hydrogenation of aromatics due to the enhanced adsorption of substrates on electron-deficient active centers [22]. Interestingly, the charge density of metal particles can be changed by the pore diameter of porous supports, which is related with the variation of pore radius of curvature [23]. It was suggested that large curvature, i.e., small pore size decreased the acidity of Al-MCM-41, which subsequently increased the electron density of metal particles. The pore wall surface curvature effect was also observed on methanol oxidization over V-MCM-41 when the vanadium loading was low [24]. The remarkable change of reaction rate as a function of pore size was attributed to the deviation in oxidization potential of vanadium which caused by changes of pore curvature.

Figure 2.1 The “interfacial” active site of a catalyst with SMSI [22].

For SMSI catalysts, the formation of specific active sites (as shown in Figure 2.1) at the interface between support and metal particles may contribute to the improved activity and selectivity of carbonyl bond hydrogenation [22]. The activation of carbonyl bond can be associated with simultaneous adsorption of carbon atom of C=O bond on metal particle and oxygen atom on the Lewis site of support [22]. Nickel nanoparticles with a thin and hexagonal morphology were prepared only when using graphite nano-fiber as the support. A high selectivity towards 1-butene in the partial hydrogenation of 1, 3-butadiene was obtained over these supported nickel catalysts [22]. The crystallites of metal nanoparticles can be oriented aligning with the symmetry of zeolite cages due to the confinement of zeolite lattice units [22]. The functional groups on support surfaces strongly interact with catalytic active centers. For example, Pt nanoparticles react with the hydroxyl groups of Al_2O_3 , resulting in a high selectivity towards butane in hydrogenation of butadiene [22]. The support surfaces can be further functionalized with various groups, e.g., amino group, and the tuned surface chemistry largely influences the catalytic performances [25].

Supports may affect the catalytic performance by directly interacting with substrates. For instance, in CO hydrogenation to methanol catalyzed by Cu supported on ZnO, the ZnO support may directly involve in the hydrogenation steps or simply serve as a hydrogen reservoir, as hydrogen molecules can dissociate over ZnO surface, giving rise to OH and ZnH [10]. Moreover, the cations of metal oxide supports also activate CO by facilitating the dissociation of CO molecules [21]. The porosity architecture of supports not only affects the diffusion and mass transfer of substrates but also restricts the alignment of reactant molecules inside the pores, leading to the different product selectivities. This confinement effect can be found in hydrogenation of molecules with different sizes over the same support (e.g., hydrogenation of cinnamaldehyde (CALD) and 3-methyl-2-butenal over zeolite supported ruthenium [26]) or hydrogenation of same substrate over supports with different pore sizes (e.g., hydrogenation of CALD over ruthenium supported by zeolite or mesoporous material [27]). In the later case, dramatic loss of selectivity over mesoporous supports was attributed to the lack of confinement on the orientation of substrate molecules.

In heterogeneous asymmetric hydrogenation, the catalytic active centers are usually in the form of metal complexes which are supported on metal oxides or polymers. Ionic interaction between support and metal complex plays an anchoring role in immobilizing the active centers [6]. Heterogenizing metal complex can also be achieved by encapsulation [28]. The so-called “ship-in-bottle” mode may exhibit higher activity and selectivity compared to the homogeneous counterpart due to the steric constraints imposed by support nanopores [28].

2.4 Preparation strategies of heterogeneous hydrogenation catalysts

Even employing the same metal and support, different preparation methods and synthesis parameters may lead to the dramatic changes in catalyst properties, e.g., dispersion of catalytic sites, metal-support interaction, metal-promoter interaction, and consequently different catalytic performances. Taking account the nature of active components, characteristics of supports and reaction mechanisms, many strategies have been developed for the synthesis of supported hydrogenation catalysts, such as impregnation [5], decomposition precipitation [10], ion exchange [29], sol-gel method [26], organometallic grafting [30], as well as most recently developed reductive deposition precipitation (RDP) [31] and microwave assisted reduction [32]. Among these preparation methods, impregnation is considered as the most facile method to prepare supported catalyst. Usually metal precursor solution is soaked (impregnated) on support, followed by drying and reducing (or calcining) [5]. Nonetheless, some important characteristics of catalysts (e.g., particle shape, size and size distributions) cannot be precisely controlled when using impregnation method [32].

By adding precipitating agent into the slurry containing support and metal precursor, metal cations can precipitate and homogeneously deposit on the support surfaces [10]. Alkalis, such as sodium hydroxide [33], sodium carbonate, oxalate [10] and urea [34] are commonly selected as precipitating agents. High pH value gives rise to a strong interaction between metal components and support surfaces [33]. Decomposition and precipitation of metal precursors in gas phase afford uniformly distributed metal precursors on support surfaces even at high metal loadings [27]. Ion-exchange has been established as a facile method to prepare supported metal

nanoparticles with high dispersions and narrow particle size distributions [29]. In sol-gel method, homogeneous solution containing all precursors including support materials is chemically transformed to a solid catalyst [26]. This sol-gel method allows an close contact of active centers with support, leading to highly dispersed metal crystallites with high activity and stability [26]. When metal complexes (e.g., acetylacetonate complexes) are employed as precursors, metal ions can be grafted (i.e., covalent bonding or coordinating) onto supports in the presence of certain surface functionalities such as carboxylic groups [30]. This organometallic grafting approach enables the immobilization of ultra-small sub-nanometer particles (< 1 nm) with high stability [30].

Figure 2.2 Preparation of bimetallic catalysts based on RDP which affords close contact between promoter and active center.

For bimetallic catalysts, it was found that the promoting effect of the second metal is not pronounced unless the promoters are adjacent or adhesive to the main active sites [35]. Aiming at achieving the close contact between primary active centers and promoters, RDP method was derived (see Figure 2.2) [31], in which the second metal was reduced by hydrogen atoms adsorbed on pre-formed parent metallic particles, affording the formation of promoter islands on the surfaces of active particles. Thus, the promoters can effectively affect the catalytic activities of the main active sites and

specifically interact with reactants [31]. In recent years, microwave assisted reduction method has been attracting increasing attention due to its intensive and uniform heating capability and short reduction time [32, 36, 37]. Under the microwave assisted heating, homogeneous nucleation of colloid metal particles can take place in a few minutes. The reducing reagents (usually diols) also act as stabilizers of metallic colloids, preventing the formation of large particles [37].

Some synthesis factors, including the types of metal precursors, reducing reagents, pretreatments, temperature of reduction/calcination, aging of catalyst etc., may affect the catalytic properties of resulting catalysts. Metal chlorides and nitrates have been widely used as precursors for active metal/metal oxide components [27]. Different from nitrate precursors, starting with metal chlorides may result in the residue of chlorine in the catalysts, which have several effects on the properties and performances of catalysts, e.g., decreasing the metal dispersion, blocking the interactions between metal particle and reducible metal oxide support, or even leading to chlorine-containing products [27]. Besides the metal precursors, reducing reagents also play a role in determining the catalytic properties. Investigation on the Pt-Co bimetallic catalysts reduced by various reducing reagents (H_2 , KBH_4 and $HCHO$) revealed that both selectivity and activity for hydrogenation of CALD were dramatically improved when using KBH_4 as the reducing agent, due to the synergic effect of Pt-Co-B [38].

Pretreatment of catalysts (e.g., pre-reduction or calcination) is usually necessary to induce the formation of alloy at the boundary between metal particle and reducible metal oxide support, or to remove undesired functional groups from support surfaces

[27]. Calcination can decrease the acidity of catalysts supported on Y zeolite or MCM-41 mesoporous molecular sieves [27]. Reduction temperature is an important synthesis parameter in determining the reduction degree, particle size and alloy composition [27]. Correlation between catalytic performance and reduction temperature was established in crotonaldehyde hydrogenation over Pt supported on ZnO [27]. The decrease in activity and simultaneously increased selectivity were contributed by the formation of Pt-Zn alloy at high reduction temperatures. Inspired by the improved selectivity caused by catalyst deactivation in gas phase hydrogenation, aging of catalysts in organic stream prior to the hydrogenation was carried out, resulting in the enhanced selectivity accompanied by the loss in activity [27].

Figure 2.3 Strategies for heterogenizing homogeneous catalysts.

Asymmetric heterogeneous catalysts are usually prepared by immobilizing the asymmetric homogeneous metal complex on certain support surfaces via grafting (covalent bond), ionic interaction or encapsulation (as shown in Figure 2.3) [28]. Anchoring metal complex on support via covalent bonding may prevent the leaching of active components to a large extent [28]. However, the catalytic results of a “free” metal complex after heterogenization are unpredictable because ligand modification is inevitable after linking the catalyst with support via covalent bond [39]. This

drawback is appreciable when rapid ligand dissociation is necessary for certain catalytic processes [39]. Alternatively, immobilizing homogeneous catalysts by ionic interaction between metal complexes and supports may avoid ligand modification, which retains the chemical status of the “free” active centers [40]. Nonetheless, leaching of metal complexes seriously occurs during catalytic reactions [6]. Another interesting heterogenization method is to encapsulate homogeneous catalysts in the pores of porous materials such as zeolites and mesoporous materials [28]. This so called “ship-in-bottle” configuration largely minimizes the variation of free metal complex catalysts except the steric confinement exerted by pore wall surfaces [28]. By confining homogeneous catalysts inside the pores of porous support, enhanced catalytic performances were reported as a result of the spatial congestion around the active centers [39].

As discussed above, the catalytic performance of a catalyst is determined by many factors. To investigate the effects of several factors simultaneously, design of experiments (DoE) is a good approach to allocate experimental points in the factor space with a rational coverage, leading to an efficient optimization procedure [41]. DoE is also an indispensable tool to screen reaction conditions such as temperature, pressure and reaction time [41]. Based on the principles of DoE including randomization, replication, blocking and efficiency, various of DoE methods have been developed, such as fractional factorial design [42], Latin hypercube sampling (LHS) [43], uniform design (UD) [44] and Hammersley sequence sampling (HSS) [45]. Factorial design of experiments has been applied to optimize a Co based catalyst for CO oxidization [46]. In the optimization of *trans*-stilbene epoxidation catalyzed by

zeolite supported Co catalysts, LHS was chosen as a preferred DoE method due to its simple implementation and good performance [41]. Correlations between catalyst properties and synthesis parameters were constructed with the aid of a custom experimental design [47].

2.5 Reaction parameters and natures of substrates

The reaction parameters such as temperature, pressure, concentration of reactants, and solvents can dramatically affect the catalytic performances. The preferential reaction parameters are also helpful for designing an effective catalyst. For example, in a high temperature gas phase hydrogenation process, stability and resistance against poison may be the most important criteria for a superior catalyst. Pt nanoparticles have been encapsulated in porous silica layers, affording a core-shell structure, which enables attaining the morphology of Pt metallic nanoparticles at 750 °C [48]. For hydrogenation reactions taking place in solutions, engineering on the structure of catalysts is usually inevitable in order to minimize the mass transport resistance [49]. For instance, mesoporous materials are more suitable for hydrogenation of bulky organic substrates compared with zeolitic materials which suffer from internal diffusion limitation due to their small pore sizes [27].

Structure of substrates may also influence the selectivity and activity over heterogeneous catalysts by means of electronic and inductive effects of substrates and the adsorption mode of substrates [27]. Benzaldehyde hydrogenation was faster than that of butanone over Pt/SiO₂ catalyst, which was explained as an inductive effect of the phenyl group, lowering the bonding strength of carbonyl on the metal surface [27]. For the selective hydrogenation of unsaturated aldehydes, the selectivities towards

unsaturated alcohols decrease as following sequences: CALD > 3-methylcrotonaldehyde > crotonaldehyde > acrolein [50]. Therefore, it is necessary to consider the nature of target reactant during the catalyst design. In the hydrogenation of 3-methylcrotonaldehyde catalyzed by supported Pt, it was found that the closely packed structure of Pt (111) surface imparts a steric hindrance to the methyl groups in vicinity of C=C bond, leading to a good selectivity towards unsaturated alcohol [51]. It has been generally accepted that large Pt particle size may promote the formation of cinnamal alcohol in CALD hydrogenation by preventing the close approach of aromatic ring nearby C=C bond [13]. The structural effect of substrate is common for asymmetric hydrogenation reactions. Small changes in the moieties of substrate may result in the variation of enantio-excess [1], which can be partially attributed to the small energy difference (15 kJ/mol) between the transition states of enantiomers [28]. In order to enlarge this energy difference, it is necessary to study the structure of substrate, which guides the design of chiral ligands [52] or asymmetric modifiers for metal nanoparticles [53].

2.6 Selective hydrogenation of α , β -unsaturated aldehyde over heterogeneous catalysts

Selective hydrogenation of α , β -unsaturated aldehyde is a critical step in the large scale production of fine chemicals, especially in fragrance [54], food [55] and pharmaceutical industries [56]. It is helpful to understand the reaction features of selective hydrogenation of α , β -unsaturated aldehyde in order to design an effective catalyst. Scheme 2.4 shows the scheme of hydrogenation of a typical α , β -unsaturated aldehyde—CALD. Hydrogen atoms can be added to C=C bond, C=O bond or both of

them, leading to the formation of saturated carbonyl (hydrocinnamaldehyde, HALD), unsaturated alcohol (cinnamal alcohol, CALC) or saturated alcohol (hydrocinnamal alcohol, HALC), respectively [56].

Scheme 2.4 Hydrogenation scheme of CALD.

According to these reaction pathways, hydrogenation of α , β -unsaturated aldehyde is usually classified as chemo-selective hydrogenation. Nevertheless, the term of region-selectivity is also applicable to this particular reaction because the selectivity depends on the hydrogen addition at a given position in this conjugate system [13]. Generally, selective hydrogenation of α , β -unsaturated aldehyde to form the saturated aldehyde is relatively easier compared to the formation of the corresponding unsaturated alcohol due to the thermodynamically favorable hydrogenation of C=C double bond (ca. 35 kJ/mol) [27]. In gas phase hydrogenation, isomerization of unsaturated alcohol to saturated aldehyde is common [57, 58]. The kinetics of isomerization in crotonaldehyde hydrogenation was carefully investigated and the results revealed that isomerization may take place regardless of the presence of hydrogen [57]. On the other hand, isomerization in liquid phase hydrogenation is rarely reported [59]. Hydrogenolysis of C-O bond was also observed in gas phase hydrogenation over a platinum single crystal [51]. In addition to the products of

hydrogenation, by-products due to the condensation of unsaturated compounds or dehydration of alcohols can also be found [56]. Therefore, it remains as a challenge to design a good catalyst with high selectivity towards the desired product, e.g., unsaturated alcohol.

For the rational design of a heterogeneous catalyst, many factors can be controlled or modified aiming to promote the catalytic properties, such as the selection of primary active metal centers, promoters, supports and preparation methods. Early studies demonstrated that different metals showed different selectivities towards unsaturated alcohols. For example, the selectivities to CALC over various metals follow a sequence: Os > Ir > Pt > Ru > Rh > Pd [13]. Theoretical calculations revealed that the specific selectivity of a given metal can be related to the radial expansion of its *d* band, larger *d* band results in more pronounced repulsion between metal atom and C=C bond, and consequently a higher possibility of C=O bond hydrogenation [3]. In addition to the intrinsic property of a metal, the size and morphology/structure of metallic active site also play vital roles in determining the selectivity of hydrogenation. It has been reproducibly substantiated in CALD hydrogenation that large metallic nanoparticle size is beneficial to the selectivity towards unsaturated alcohol [12, 60]. This particle size effect was attributed to the significant repelling force between large particle and phenyl group of CALD, which hinders the approaching of C=C bond to the metal surface (as shown in Figure 2.4) [60]. It has been found that hydrogenation of α , β -unsaturated aldehyde over different facets of Pt single-crystal (Pt (111) or Pt (110)) led to distinct product distributions, due to the variation of packing mode of Pt atoms [51, 61].

Figure 2.4 Adsorption of CALD on a small metal particle (left) and large non-curved particle (right) [60].

One of the most efficient ways to improve the catalytic properties is to introduce a second metal (a promoter) to the main active sites. The promoters can be a metal [62], metal oxide [12] or ion. For the bimetallic active center composed by a alloy, the second metal acts as an electron donor to increase the electron density of main active metal, which inhibits the adsorption and hydrogenation of C=C bond [62]. The promoting effect of metal oxide species deposited on the surface of main active metal arises from the electrophilicity of the positively charged promoter metal which may adsorb and activate the C=O bond via its lone electron pair of oxygen [12]. Adding metal ions to promote the catalytic performance of primary metal center was also reported [63]. During the hydrogenation, promoters may be reduced and deposited on the surface of main active metal; electron transfer from promoter to active center affords the uneven distribution of electrons, i.e., forms a electron deficient promoter and a electron rich active center [63]. Subsequently, C=O bond is activated by the electropositive promoter species, while C=C bond is repelled by the active center with a high electron density. Thus, this synergistic interaction between primary active center and promoter (as shown in Scheme 2.5) greatly improves the selectivity towards unsaturated aldehyde [64].

Scheme 2.5 Hydrogenation of CALD over Pt promoted by a second metal [63].

The role of a support material in selective hydrogenation of unsaturated aldehyde depends on several aspects, such as metal-support interaction [13], surface properties of support [65] and the steric effect imposed by porous supports [66]. Support may act as a “ligand” donating electrons to metal particles, e.g., electron transfer from graphite to the anti-bonding orbitals of Pt nanoparticles was evidenced by the expanded Pt crystal lattice and decreased adsorption coefficient of benzene and toluene [13]. The initial selectivity towards unsaturated alcohol over Pt/graphite is significantly higher than Pt/C due to the weak electron-donating capability of active carbon. It is noteworthy mentioning that the enriched electron density over a metal cluster only lowers the possibility of C=C bond adsorption and simultaneously accelerates the hydrogenation rate of C=O bond. Therefore, increase in the selectivity towards unsaturated alcohol is not accompanied by the improved activity [13]. Similar but less pronounced electronic effect was also observed over Pt supported on carbon nano-fiber (CNF) [65]. Interestingly, the activity of Pt/CNF in CALD hydrogenation was increased by a factor of 25 after eliminating the oxygen-containing groups from CNF surfaces, which was attributed to the improved affinity/adsorption between support and CALD [65]. When metal nanoparticles were confined in pores or channels of a porous support, the spatial constrain imposed by the pore wall surfaces can orientate

the adsorption geometry of reactants and thus change the selectivity [66]. Metal nanoparticles confined in Y zeolite cages showed a higher selectivity towards unsaturated alcohol compared to those supported on active carbon [66]. Large molecules are more sensitive to this steric effect of support than small ones, e.g., the selectivity to unsaturated alcohol is remarkably higher for hydrogenation of CALD than that of 3-methylcrotonaldehyde over zeolite confined metallic nanoparticles [66]. However, micropores of zeolite support may hinder the transport of reactants and products, resulting in a fairly low catalytic activity [13].

Several synthesis methods have been developed to prepare supported catalysts for selective hydrogenation of α , β -unsaturated aldehyde, such as impregnation, deposition precipitation, ion-exchange, gas or liquid phase deposition and sol-gel method [27]. The influence of preparation methods on catalytic performance is mediated by modifying catalyst properties involving metal particle morphologies, dispersion of active components, metal-support interaction etc. Silver nanoparticles with dominating fraction of dense (111) surface plane were prepared by impregnation and sol-gel methods [67]. Increasing the exposure of Ag (111) plane improved the selectivity to unsaturated alcohol by limiting the coordination of C=C bond on this specific crystal plane. Confinement of metal nanoparticles inside the cages of zeolitic materials was achieved by ion-exchange, and the high selectivity to unsaturated alcohol was obtained due to the steric constrain of limited space between metal nanoparticles and pore wall surfaces [66]. In contrast, Ru nanoparticles loaded on silica mesoporous material (MCM-41) via ion-exchange showed a high activity in CALD hydrogenation along with a remarkably poor selectivity towards CALC [68].

Highly dispersed metallic active centers can be loaded on an appropriate support (e.g., silica and alumina oxide) via gas- or liquid-phase deposition [69]. Different from the case of impregnation approach, the superior catalytic property of catalysts prepared by deposition was contributed by the ligand-exchange between metal precursors and support surfaces.

Deposition co-precipitation is regarded as an effective method to prepare supported bimetallic catalysts. Hydrogenation of crotonaldehyde was carried out over Ni-Cu/Al₂O₃ prepared by co-precipitation of Ni and Cu nitric salts in the presence of alkali (as shown in Figure 2.5) [70]. The catalytic performances of this bimetallic catalyst were explained by the different electron properties of hydrogen adsorbed on nickel and copper. It was suggested that the hydrogen atoms adsorbed on copper were more prone to donating electrons (i.e., in a more hydridic form) than those adsorbed on nickel. Nonetheless, hydrogen can transfer electrons to the empty *d* orbitals of nickel while *d* orbitals of copper are full. Therefore, these hydrogen atoms with different electron status may be suitable to hydrogenate the carbonyl groups (as shown in Figure 2.5) rather than to react with less polarized C=C bonds [70]. However, it is expected that the synergistic metal-metal interaction of bimetallic catalysts can hardly be controlled by co-precipitation procedures as two precursors precipitate independently to a certain extent. Therefore, the RDP method was developed to prepare bimetallic catalysts for selective hydrogenation of α , β -unsaturated aldehyde [31]. Positively charged promoters on the noble metal surface act as an electron pair acceptor to interact with the oxygen atom of carbonyl group, and consequently improve the selectivity towards unsaturated alcohol [31].

Figure 2.5 Hydrogen adsorbed on Ni and Cu with different electronic properties in crotonaldehyde hydrogenation.

Reaction conditions remarkably affect the performance of a given catalyst. In general, the activities of hydrogenation catalysts increase with increasing the reaction temperature [71]. However, poor hydrogenation rates were also observed at a elevated temperature [72], which is due to the poison of CO formed by decarbonylation of α , β -unsaturated aldehyde. In gas phase hydrogenation, increase in the total pressure not only accelerates the reaction rate but also changes the adsorption of reactants [73]. A high total pressure results in the enhanced selectivity to unsaturated alcohol as a consequence of deviated adsorption mode of α , β -unsaturated aldehyde on metal surfaces [73]. In liquid phase hydrogenation, by changing the hydrogen pressure, the selectivity towards unsaturated alcohol may decrease [72], remain constant [74] or pass through a maximum [75]. In the hydrogenation of citral, increasing hydrogen pressure did not change the selectivity to nerol and geraniol, suggesting the same reaction orders of these two parallel hydrogenating routes [74].

Solvent effects have been extensively investigated for hydrogenation of α , β -unsaturated aldehyde [49]. The hydrogenation of C=O bonds is preferable in polar solvent, whereas C=C bond is prone to be reduced in a non-polar solvent [76]. Different solvents may have distinct hydrogen solubility, although a high hydrogen solubility does not necessarily associate to a high hydrogenation rate due to the fact that many other factors should be considered when solvent is changed [77], e.g., by-products formation [75]. These by-products may adsorb on active sites, resulting in the rapid catalyst deactivation. Less formation of by-products were reported by using bulky alcohol (e.g., 2-methyl-2-propanol) as the solvent compared to the smaller alcohols such as methanol, ethanol and 2-propanol [75]. Water content in a solvent may also affect catalytic performance. A dramatic increase in reaction rate was observed by changing the water/ethanol ratio in CALD hydrogenation over cobalt borides [78]. Moreover, other solvents including supercritical carbon dioxide [79] and ionic liquids [27] are applied to the hydrogenation of α , β -unsaturated aldehyde, regarding of their environmentally friendly characteristics.

2.7 Chiral mesoporous material—a novel support of asymmetric catalysts

Asymmetric hydrogenation, a more feasible way to produce enantio-enriched compounds at a preparative scale, is essentially crucial for pharmaceutical industries because enantiomers exhibit remarkably different physiological properties [80]. Several chiral catalysts with high enantioselectivities have been prepared and the corresponding immobilizations of these chiral catalysts on achiral supports were reported. Nonetheless, investigations on the other catalyst configuration, e.g., the chiral support along with the achiral active sites are limited, although the influence of

a chiral carrier on asymmetric catalysis can be anticipated. The asymmetric hydrogenation catalyzed by palladium nanoclusters supported on silk (a natural chiral carrier) may be regarded as a good example of asymmetric catalysis over achiral active sites supported on chiral carriers (see Figure 2.6a) [81]. Chiral discrimination capability of enantio-pure crystals of inorganic materials has long been recognized. In 1936, Tsuchida et al. reported the partial resolution of several racemic cobalt complexes on chromatographic columns packed with d- or l-quartz powder [82]. Forty years later, Bonner and co-workers elaborately investigated the selective adsorption of amino acids and their derivatives using d- or l-quartz powder (see Figure 2.6c), and 12.4% of the enantiomeric enrichment was claimed [83]. Interestingly, Sato et al. found that chiral crystal of inorganic materials such as sodium chlorate [84] and quartz [85] can induce the high enantioselectivity in asymmetric autocatalytic reaction (see Figure 2.6b).

Figure 2.6 Applications of naturally chiral materials on asymmetric catalysis and enantio-selective discrimination.

Recently, the chiral unit in quartz has been identified to be the SiO_4 segment helix [86]. Si-O-Si bond in amorphous silica is more flexible than in quartz, and thus it is reasonable to suggest inducing chirality to amorphous silica using proper directing agents. Fireman-Shoresh et al. reported the synthesis of amorphous chiral silica materials using chiral cationic surfactants as templates, and subsequently demonstrated that both template-doped and template-free chiral silica matrixes can enantio-selectively adsorb enantiomers [87, 88]. They also indicated that it was “no surprise” that chiral surfactants induced the chirality to the building blocks of amorphous silica (SiO_4 tetrahedra and $\text{Si}(\text{OSi})_4$) [89]. Furthermore, the same group proved the formation of chiral silica using an induced circular dichroism (ICD) method [89]. Similar observation was also reported on the synthesis of left- and right-handed helix silica nano-rods [90].

Figure 2.7 (a) Chiral zeolite with helix arrangement of cages [91]; (b) SEM image and scheme of helix channels of chiral mesoporous silica [92]; (c) Proposed formation mechanism of chiral mesoporous silica [92].

The chirality of porous materials may be more pronounced than that of bulk or amorphous chiral solids, regarding to their remarkably high specific surface areas. Chiral structure has been found in beta zeolite, although the polymorphs with opposite chirality always grow together [93]. Few enantio-pure zeolites have been obtained successfully [91, 94]. However, none of them have found application in any enantioselective process due to the fact that either they are thermally unstable after removing template or the limitation of small channel dimension. In 1992, mesoporous silica materials were discovered by Mobil researchers [95, 96]. The major advantage of mesoporous materials is that their pore sizes (2-30 nm) are generally much larger than those of microporous materials, which allows the inner surface accessible to bulky molecules [97]. Recently, the discovery of chiral mesoporous materials attracts our attention [98]. Different from achiral mesoporous silica materials, the chiral mesoporous silica is constructed by either right-handed or left-handed helix channels [92, 99-104].

The formation of helical channels was attributed to the templating effect of chiral surfactants. The chiral anionic surfactants interacted with positively charged silica precursors, transferred the chirality of micelles to the silica precursors. Nevertheless, subsequent investigations found that chiral surfactants were not necessary for the formation of helical structures [99-102]. Several synthesis parameters controlled the self-assembly of achiral template and silica precursor, resulting in the mesoporous silica with helical morphology [104]. Thermodynamic explanation for the formation of chiral channels was developed other than the chiral transcription mechanism. Yang et al. proposed that the helical mesostructure depended on the competition between

decrease in the surface free energy (ΔG_S) and the increase in bending energy (ΔG_B) [101]. They suggested that the formation of helical channel will be favorable as long as the particle length is larger than the diameter. More recently, an entropy-driven model for understanding the helical conformation of long molecular chains in a crowded environment was proposed to explain the formation of helical mesostructured silica [102]. Up to now, there are insufficient reports on the chiral discrimination or catalysis based on these chiral mesoporous silica with helix channels.

2.8 Asymmetric hydrogenation based on phosphorous ligands

Metal complexes composed by an active center (metal ion), one or more chiral ligands and anions can serve as effective homogeneous catalysts which are able to add hydrogen atoms to unsaturated bonds. The catalytic properties of these catalysts mainly depend on the nature of ligands for any particular metal. Up to now, the most extensively applied catalysts are Ru, Rh and Ir complexes coordinated with phosphorus ligands [52]. Many research efforts have been devoted on designing various kinds of phosphorus ligands. However, only a limited number of ligands are proved to be commercially applicable in industrial process and these ligands are usually referred as “privileged ligands” [105]. Some of these privileged ligands and their acronyms are shown in Scheme 2.6. By analyzing the structure of these ligands, some general principles can be drawn for designing an effective ligand [52]. For example, a privileged ligand is bidentate and has C_2 symmetry. Phosphorous atom should be bonded with aryl or bulky alkyl groups. The structure of a superior ligand should have certain flexibility to afford a high activity as well as sufficient rigidity to induce enantioselectivity [52]. Based on these privileged ligands, significantly high

activity and stereoselectivity have been achieved in asymmetric hydrogenation of C=C, C=O, and C=N bonds [106].

Scheme 2.6 Privileged bidentate and monodentate ligands and their typical coordination configurations.

For a long period of time (over last 30 years), enantioselective hydrogenations were exclusively based on bidentate phosphorous ligands, as it was assumed that the rigidity of a metal complex formed using bidentate ligands was a crucial factor for the chiral induction and enantioselectivity [107]. Different from bidentate and multidentate ligands, a monodentate ligand possesses only one atom that coordinates with the metal ion within the coordination sphere, such as chiral monodentate phosphines [107] and monodentate phosphoramidites [108]. Usually, this kind of metal complex consists of two isolated monodentate ligands as shown in Scheme 2.6. Although the structure of monodentate complex is less rigid than that of bidentate one,

two or more moieties of phosphoramidite monodentate ligands are usually large enough to restrict the freedom of conformation in the coordination sphere [109]. Remarkably high enantiomer excess ($ee > 99.8\%$) has been achieved using phosphoramidite—rhodium complexes in the asymmetric hydrogenation of olefins [109]. Monodentate phosphine ligands were also successfully applied to the asymmetric hydrogenation of C=O bonds [107]. Another advantage of monodentate phosphoramidites is that their synthetic route is relatively simple, and thus screening a large library of ligands with the aid of robot is applicable [108]. It has been shown that the catalytic performances of 96 phosphoramidite ligands can be verified in two days [108].

An intriguing observation on monodentate ligands is the influence of ligand/metal (L/M) ratio on asymmetric reactions. van den Berg et al. showed that the catalytic activity ceased when the L/M ratio was increased to 3 in the Rh catalyzed hydrogenation of olefin [110]. The reaction rate increased and ee value remained constant over the L/M range from 1 to 2. These results implied that metal complex carrying only one single monodentate ligand may also be active [110]. Another distinctive feature of monodentate ligands is that mixture of ligands gives rise to the presence of hetero-complex (ML_1L_2) in addition to the corresponding homo-complexes (ML_1L_1 and ML_2L_2). By screening various hetero-complexes bearing monodentate phosphorous ligands, Pena et al. suggested that some hetero-complexes were more active and enantioselective than homo-complexes [111]. However, the preparation of ML_1L_2 in pure form in the solution is challenging because of the equilibrium of ligand-metal coordination [112].

Figure 2.8 Immobilization of monodentate ligands via copolymerization (a) [7] or ion-pair interaction (b) [40].

Due to the economical and environmental concerns, many techniques have been developed for heterogenizing the homogeneous catalysts on appropriate carriers, such as covalent bonding [7], ion-pair formation [40], and entrapment in nanopores [28] because the recovery of these expensive asymmetric catalysts is difficult in the homogenous mixture of catalyst and reaction solution. Compared to the rapid development of monodentate ligand for homogenous catalysts, reports on the immobilization of these novel catalysts are limited. Polymer-supported phosphoramidites were prepared by introducing carbon-carbon double bonds in the amine moiety (see Figure 2.8a) [7]. Simons et al. reported the anchoring of a monodentate ligand—Rh complex on mesoporous aluminosilicate Al-TUD-1 by ionic interaction between aluminum and rhodium (see Figure 2.8b) [6, 40]. Although the superior *ee* value and conversion in hydrogenation were achieved in a water solution, the leaching of catalysts was inevitable.

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Chapter 3 Techniques of Characterization, Synthesis, and Catalytic

Hydrogenation

Characterization techniques are indispensable to unveil the chemical and physical properties of catalysts which may control the catalytic performances. With the aids of advanced characterization technologies, one can study the characteristics of catalysts on a molecular/atomic level, and thus catalyst design can be conducted in a rational way. To appropriately take the advantage of characterization tools, it is necessary to understand the fundamental concepts of the techniques which will be briefly described in this chapter as well as the synthesis methodologies of the catalysts and support materials in this thesis.

3.1 Characterization techniques

3.1.1 Characterization of catalyst morphologies and structures

X-Rays diffraction (XRD) is a useful technique to characterize the lattice/long range structures of crystalline (e.g., metal particles [1]) or other ordered materials (e.g., mesoporous materials [1] and zeolites [2]). The compositions of metals and alloys can also be studied by XRD measurement. Additionally, the average particle size of crystalline can be estimated based on the width at half maximum of well resolved diffraction peaks using Scherrer's equation [3]. Furthermore, XRD is widely used to characterize the nano-structure of support materials. For mesoporous molecular sieves, XRD signals are not derived from uniform arrangement of atoms as in crystals, but from the ordered nano-sized pore walls [1]. In this thesis, XRD measurements were conducted on a Bruker AXS D8 X-ray diffractometer (Cu K α , λ =1.542Å, 40 KV, 30

mA) with a resolution of 0.02° (2θ) for both high angle (10 - 80°) and low angle (1 - 8°) measurements.

Physical adsorption (physisorption) of nitrogen is another useful method to characterize porous materials. Several important parameters of porosity such as specific surface area, pore volume, pore size and pore size distribution can be extracted from the isotherms of adsorption and desorption. Usually, the specific surface area can be obtained from Brunauer-Emmett-Teller (BET) method [4]. Pore volume and pore size can be calculated by Barrett-Joyner-Halenda (BJH) method [5]. In this PhD work, nitrogen adsorption-desorption isotherms were measured at 77 K on a static volumetric instrument Autosorb-6b (Quanta Chrome). Prior to the tests, samples were degassed at 473 K to a residual pressure below 10^{-4} Torr. A Baratron pressure transducer (0.001 - 10 Torr) was used for low-pressure measurements. The pore size and pore size distributions were calculated using the desorption branch of isotherms.

Scanning electron microscope (SEM) and transmission electron microscopy (TEM) enable the direct observations on catalyst morphologies and structures. In this PhD work, the SEM image was obtained on a JEOL Field Emission Scanning Electron Microscope (JSM-6700F-FESEM). Prior to the measurements, the samples were deposited on a sample holder using an adhesive carbon tape and then decorated with gold through sputtering. TEM was performed on JEOL JEM-2010, operated at 200 KV. The samples were suspended in ethanol and dried on holey carbon-coated Cu grids. As a complement of SEM and TEM observations, dynamic light scattering (DLS) was also employed to measure the particle sizes and size distributions of

supports. Particles were well dispersed in ethanol prior to each test which was conducted on a 90Plus particle size analyzer (Brookhaven Instruments Corporation) at 298 K.

3.1.2 Characterization of catalyst active sites

Many sophisticated and powerful characterization methods have been widely adopted to investigate the properties of catalytic active centers, such as electron paramagnetic resonance (EPR) spectroscopy, hydrogen temperature programmed reduction (H₂-TPR), X-ray absorption near edge structure (XANES) and X-ray photoelectron spectroscopy (XPS) etc. In this PhD work, XPS was employed to study the chemical state of metal nanoparticles. The measurements were conducted on a VG Escalab 250 spectrometer equipped with an Al anode (Al K α = 1846.6 eV). The background pressure in the analysis chamber was lower than 1×10^{-7} Pa. Measurements were performed using 20 eV pass energy, 0.1 eV step and 0.15 min dwelling time. Binding energy correction was carried out using the C_{1s} peak of adventitious C at 284.6 eV. Inductively Coupled Plasma (ICP) technique was used to determine the contents of metals. Samples were prepared by Milestone microwave laboratory system and analyzed by Perkin-Elmer Dual-view Optima 5300 DV ICP-OES (Optical Emission Spectrometry) system.

Figure 3.1 Working scheme of a typical electrochemistry measurement. The waveform is performed by a potentiostation. E_1 , E_2 and v are the starting potential, reversal potential and scan rate, respectively. C, W and R stand for counter, working and reference electrode, respectively. Gas may be introduced in electrolytic cell regarding the requirement of experiment.

In addition to the traditional characterization methods as mentioned above, electrochemistry measurements including cyclic voltammetry (CV) and carbon monoxide (CO) stripping were chosen to investigate the properties of support materials and catalytically active metal nanoparticles. These methods are common in the characterization of electro-catalysts and they are extremely surface sensitive characterization techniques [6]. In this PhD work, the electrochemical signals were correlated with the chemical properties of catalysts and their catalytic performances. Both CV and CO stripping can be classified as potential sweep methods in which the current is recorded while potential of electrode is linearly changed with time in a selected potential range. Figure 3.1 shows the experimental setup and working scheme of a typical electrochemistry measurement. CV measurements are remarkably

sensitive to redox reactions involving adsorption of products and reactants. If highly dispersed metal nanoparticles are prepared as a working electrode (e.g., Pt nanoparticles supported on active carbon), several redox signals caused by the surface characteristics of active centers may be detected. These signals provide information of chemical state or environment of metal active centers. A typical CV profile of Pt electrode with high surface area in H₂SO₄ water solution is shown in Figure 3.2. The electrochemical active surface (EAS) area of Pt can be calculated from the amount of exchanged charges during the electrochemical adsorption (Q') and desorption (Q'') of hydrogen on metal surfaces by using Equation 3.1 [7]:

$$\text{EAS-H} = Q_H / ([\text{Pt}] \times 0.21) \quad (3.1)$$

in which, [Pt] is the unit Pt loading at working electrode (unit: mg/cm²); Q_H is the average value of Q' and Q'' (unit: mC/cm²); 0.21 is the charge for oxidization of 1 atom layer of hydrogen on unit Pt surface (unit: mC/cm²).

Figure 3.2 A typical CV profile of a Pt electrode with high surface area in H_2SO_4 . Q' and Q'' are the amount of exchanged charge for the electrochemical adsorption and desorption of hydrogen on the surface of Pt, respectively. The hatching area can be attributed to the double layer charge [6, 7].

However, it was found that the electrochemical information derived from CV measurement is limited when conventional catalysts are characterized due to the low loading of metals and large background caused by supports. As a consequence, the peaks of hydrogen adsorption and desorption can hardly be discerned in some cases. Therefore, another potential sweeping method—CO stripping was employed to probe the electrochemical status of active centers and calculate the EAS. In a CO stripping experiment, CO is introduced in the electrolytic cell and adsorb on the surface of metals at a low potential, subsequently the potential sweeps as a function of waveform of conventional CV. During the positive sweeping, CO can be oxidized to CO_2 and stripped from the surface of metal (e.g., Pt) as shown in Figure 3.3 (left). By deducting the contribution of CO free catalyst (i.e., the signal of second CV scan after removal of adsorbed CO in the first scan), the onset and peak potential of CO stripping as well

as the charge exchanged during CO oxidization (Q_{CO}) can be measured (see Figure 3.3 right). The positions of onset and peak potentials of CO oxidization can be used to evaluate the properties of metal particles in terms of oxidization capability. Lower onset and peak potentials indicate that CO can be more easily oxidized to CO_2 [7]. Similar with CV measurement, the EAS area of metal can also be obtained based on the Q_{CO} value by using Equation 3.2 [7] :

$$EAS-CO = Q_{CO}/([Pt] \times 0.484) \quad (3.2)$$

where $[Pt]$ is the unit Pt loading at working electrode (unit: mg/cm^2); Q_{CO} is the charge exchanged during CO oxidization (unit: mC/cm^2); 0.484 is the charge for oxidization of 1 atom layer of CO on unit Pt surface (unit: mC/cm^2).

Figure 3.3 Scheme of CO stripping on a Pt particle and a typical CO stripping profile of Pt supported on CNTs in a KOH water solution. Q_{CO} is the charge exchanged during CO oxidation.

In this PhD work, CV and CO stripping were carried out in a 1.0 M KOH solution at 50 mV s^{-1} (Princeton Applied Research, VersaSTAT 3 Potentiostat/Galvanostat). The working electrode was prepared by dropping $30 \mu\text{L}$ of the catalyst ink onto a glassy carbon electrode. The ink was prepared by ultrasonically mixing 2 mg of catalyst sample with 3 mL of 0.025 wt.% Nafion in ethanol solution. Pt foil and Hg/HgO (1.0 M KOH) electrodes were used as the counter and reference electrodes, respectively. All the potentials in the present study are given versus the Hg/HgO (1.0 M KOH) electrode. The potentials of CV test ranged between -0.8 and 0.3 V. CO stripping was performed as follows: after purging the solution with nitrogen for 20 min, gaseous CO was bubbled for 15 min to form the CO adlayer on the catalysts while maintaining the potential at -0.8 V. Excess CO in the solution was expelled by purging with nitrogen. CO stripping voltammetry was also recorded in a range between -0.8 and 0.3 V.

It was suggested that “the most sensitive probe of a catalyst is a catalytic reaction. [8]” In this study, competitive hydrogenations of toluene and benzene were carried out to probe the electronic properties of Pt nanoparticles. By measuring the relative hydrogenation rates of toluene and benzene, an equilibrium adsorption constant ($K_{T/B}$) can be derived from Equation 3.3, in which P_T/P_B is the ratio of toluene and benzene partial pressures, r_B^0 is the reaction rate of pure benzene, r_B is the reaction rate of benzene at P_T/P_B [9]. $K_{T/B}$ is temperature-dependent and independent on particle size or other effects on local geometric surface structure [8]. As toluene is a better π -electron donor compared to benzene, the larger $K_{T/B}$ value means stronger adsorption capability of toluene than that of benzene, as a result of the electron deficiency of metal particles [8]. Therefore, it is applicable to relate the electron density of active center with $K_{T/B}$ value.

$$r_B^0/r_B = 1 + K_{T/B}(P_T/P_B) \quad (3.3)$$

The procedures for toluene and benzene hydrogenations were similar to that reported by Poondi and Albert Vannice [9]. A liquid chromatography pump (Shimadzu, LC-20AT) introduced toluene and benzene into a mixer maintained at 423 K. The ratios of toluene/benzene ranged from 0 to 0.8. The gasified aromatic mixture was carried by a H_2 flow (40 mL/min) and passed through 0.02 g of catalyst pre-loaded in a down-flow quartz reactor. The reactor temperature was maintained at 308 K. The effluent gas was analyzed using a gas chromatograph (Agilent, 6890N) fitted with a HP-PONA column (Agilent) and flame ionization detector (FID). All reaction conversions were kept below 10%.

3.1.3 Characterization of chiral mesoporous silica (CMS) support materials

The helix nano-channels of CMS can be clearly observed by using TEM [10]. Nevertheless, if the chirality of a silica material is based on a single SiO_4 tetrahedron or an aggregation composed by several atoms [11], any attempt to study the chiral entity in the TEM image may lead to ambiguous explanation. In this PhD work, the chirality of CMS was evidenced by enantio-selective adsorption of enantiomers. The enantio-bias after selective adsorption was determined by circular dichroism (CD) spectroscopy which was conducted on a Jasco (Tokyo, Japan) J-810 spectropolarimeter with a 1 mm cell path length. Zeta-potential was measured on zeta potential analyzer (ZetaPALS, Brookhaven Instrument Corporation) at 313 K. Each data point was an average of 10 consecutive runs. In addition, vibrational circular dichroism (VCD) was also employed to substantiate the local chirality of the synthesized CMS. Similar to the widely applied CD spectroscopy which measures the different absorption of left and right circularly polarized radiations (denoted as LCP and RCP, respectively) in the near-ultraviolet (UV) and visible spectral regions, VCD detects the absorption difference (ΔA) of LCP and RCP in the infrared region when polarized light is passing through a chiral material (as shown in Figure 3.4) [12]. Therefore, each VCD signal has a corresponding signal in the infrared spectrum. This method is feasible to detect the chirality of solid materials.

Figure 3.4 Mechanism for the formation of CD and VCD signals.

In this PhD work, a Nicolet VCD Nexus module was coupled with a Nicolet 8700 dual-channel FTIR spectrometer. The infrared light source from the spectrometer was directed to the focus lens of the module, passing through a linear polarizer, a PEM-90 operating at 50 kHz, and then penetrated through the sample under study. A liquid nitrogen cooled MCT detector with focus lens assembly was employed. The processing electronics included a dedicated SSD demodulator with a large dynamic range to demodulate the differential signals at the modulation frequency of the PEM and two digitizers recording both the raw signal (non-demodulated) from channel A and the demodulated signal from channel B. Prior to spectral presentation, built-in deHaseeth phase correction in OMNIC was used for Fourier transformation. Powder sample was dispersed in KBr pellets and measured at a resolution of 8 cm^{-1} with 500 scans for each sample.

3.1.4 Characterization of free and immobilized chiral ligands

Nuclear magnetic resonance (NMR) is one of the most important characterization methods in organic synthesis. In this PhD work, the “free” chiral ligands were characterized by both ^1H NMR (tetramethylsilane is the internal standard) and ^{31}P

NMR (phosphoric acid is the external standard) spectra which were recorded on a 300 MHz Bruker Avance DPX 300 apparatus in deuterated solution at 298 K. Ligands anchored on silica support surfaces were investigated by *in situ* Fourier transform infrared spectroscopy (FTIR) and Diffuse Reflectance UV-visible Spectroscopy (UV-vis). *In situ* FTIR spectra ranging between 400 and 4000 cm^{-1} were recorded on a Digilab FTS 3100 spectrometer with a resolution of 0.5 cm^{-1} using KBr wafer technique. Diffuse reflectance UV-vis spectra were recorded on a Vavian Cary-5000 spectrophotometer equipped with a diffuse-reflectance accessory. The spectra were recorded in the 200-800 nm range at room temperature with BaSO_4 as reference.

3.2 *Synthesis methodologies*

3.2.1 *Materials*

$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (>37.5%, Pt basis), $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (>97%), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (>98%), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (99%), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (>98%), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (>98.5%), $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (98%), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (>98%), SnCl_2 (98%), Bis (1,5-cyclooctadiene) rhodium (I) tetrafluoroborate ($\text{Rh}(\text{COD})_2\text{BF}_4$, 99%), phosphorous trichloride (PCl_3 , 99%), KI (99 %), KCl (99 %), HCl (36-38 wt.%), KOH (99.99%), CaH_2 (95%), butyllithium (hexane solution, 1.6 M), Na_2SiO_3 (98%), N-[3-(trimethoxysilyl)-propyl]aniline (AnPTMS, 98%), sodium D-tartrate (98%), ($\pm$)-*trans*-1,2-diaminocyclohexane (DACH, 99%), L-valine (99%), D-valine(99%), D,L-valine (>99%), hexadecyltrimethylammonium bromide (CTAB), P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$), Nafion solution (5% in isopropanol and water), cinnamaldehyde (CALD, >99%), cyclohexane (99.5%), 1-butanol (>99%), ethanol (>99.5%), 2-propanol (>99%), 1,4-dioxane (99.8%), benzene (>99.9%) and toluene (>99.9%) were purchased from

Sigma-Aldrich. HNO_3 (65%), tetraethyl orthosilicate (TEOS, 98%), silica gel (for column chromatography, 40), tetradecane (>99.5%), hexamethyldisilazane (MSiN , >98%), sodium 1-(4-chlorophenyl) ethanol were purchased from Fluka. Ethyl acetate (EA, >99.5%) was purchased from Acros. Ethylene glycol (EG, 99.5%) was purchased from Sinopharm. Multi-walled carbon nanotubes (CNTs, >95%) were purchased from Cnano. Pluronic F127 ($\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$) was purchased from BASF. S-(-)-1,1'-Bi(2-naphthol) (BINOL, 99%) was purchased from Alfa. All chemicals were used as received without any further purification. Tetrahydrofuran (THF, >98%, Fluka), dichloromethane (CH_2Cl_2 , >99.8, Sigma-Aldrich), N-ethylaniline (>98%, Fluka) and triethylamine (NEt_3 , 99%, Alfa) were distilled over CaH_2 prior to the usage.

3.2.2 Preparation of Pt supported on CNTs by a microwave-assisted polyol reduction (MAPR) method

The pristine CNTs was treated with concentrated and diluted nitric acids successively following the procedures as described by Lordi et al. [13]. The concentrated nitric acid removed the amorphous carbonaceous and metallic impurities; the diluted nitric acid slowly oxidized the purified CNTs to create abundant surface functional groups, which facilitated the uniform deposition of metal precursors. To deposit Pt precursors onto pretreated CNTs surfaces, 0.1 g of CNTs was immersed in 722 μL of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ aqueous solution (20 mg/mL) and dried at 373 K in vacuum. EG (40 mL) was added to the above-mentioned Pt-CNT composite followed by sonicating for 10 min to afford a homogenous suspension. The said suspension was transferred into a three-neck flask with a condenser and placed in a microwave reactor (Sineo, MAS-II). The slurry was agitated by a magnetic stirrer and the temperature

inside the flask was monitored by an infrared sensor. The suspension was heated to 438 K in 0.5 min and kept at the same temperature for 1.5 min. After cooling to room temperature, the powder was filtrated out and washed with deionized water, followed by drying at 373 K in vacuum. The as-synthesized catalyst was denoted as Pt/CNT, the expected Pt loading is 5 wt.% and confirmed by inductively coupled plasma (ICP) measurements. Pt/CNT was pretreated at various temperatures (673, 773, 873 and 973 K) in a nitrogen flow (20 mL/min) for 2 h to remove the oxygen-containing groups from CNTs surfaces. The resulting catalysts were denoted as Pt/CNT-673, Pt/CNT-773, Pt/CNT-873 and Pt/CNT-973.

The preparations of bimetallic catalysts were similar to that of Pt/CNT but in the presence of both Pt and transition metal precursors. The Pt loading was kept at 5 wt.% and the molar ratio of Pt to promoter was 1:1. All the as-synthesized bimetallic catalysts were pretreated at 973 K in nitrogen, and were denoted as PtMn/CNT-973, PtFe/CNT-973, PtCo/CNT-973, PtNi/CNT-973, PtCu/CNT-973, PtZn/CNT-973 and PtSn/CNT-973. For comparison, Pt/CNT catalysts promoted with Fe or Co were also prepared by a conventional impregnation (IMP) method (denoted as PtFe/CNT-973-IMP and PtCo/CNT-973-IMP). Aqueous solutions of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were impregnated onto the oxidized CNTs followed by drying under ambient conditions overnight. The impregnated catalysts were pre-reduced in hydrogen flow (50 mL/min) at 473 K for 2 h and subsequently exposed to a nitrogen flow (20 mL/min) at 973 K for another 2 h.

3.2.3 Preparation of chiral cobalt complex (CCC)

CCC, Λ -[Co((+)-chxn)₃]₃I₃ (chxn = *trans*-1,2-diaminocyclohexane) was prepared following a previously reported method prior to the synthesis of CMS materials [14]. 11.43 g of CoCl₂·6H₂O was dissolved in 100 g of deionized water, followed by adding 10.33 mL of (+)-*trans*-1,2-diaminocyclohexane (DACH) and bubbling air into the solution for 4 h. The mixture was subjected to filtration and 40 mL of concentrated HCl was added to the filtrate, followed by removal of water by heating to 368 K. A green powder was obtained after overnight drying under ambient conditions. The powder was dissolved in 20 g of deionized water at 353 K, followed by adding 6.87 mL of DACH and stirring for 5 h. The red-brown precipitate was collected by filtration and dried in air before resolution.

12.53 g of above-prepared solid mixture was dissolved in 600 g of deionized water and heated to 363 K, followed by adding 4.97 g of sodium D-tartrate gradually under vigorous stirring. The mixture was cooled to room temperature, and the solids were filtered out. The filtrate comprises three stereoisomers. The resolution of CCC was achieved based on the different solubility of stereoisomers. The filtrate was cooled to 273 K, and 10.74 g of saturated potassium iodide (99%, Sigma) aqueous solution was added drop-wise. CCC precipitated first due to its lowest solubility compared to the other two stereoisomers.

3.2.4 Synthesis of CMS and achiral mesoporous silica (ACMS)

For the synthesis of CMCM-41, 0.133 g of CTAB, CCC (as-prepared, 0.013 g) and 0.12 g of Na₂SiO₃ were dissolved in 40 g of deionized water at 313 K. 0.53 g of EA was added to initiate the precipitation of silica. The molar composition of the

synthesis mixture was 1 (SiO₂): 0.36 (CTAB): 0.01 (CCC): 6 (EA): 2222 (H₂O). The mixture was allowed to age at room temperature under static condition for 2 days. The products were recovered by filtration and dried under ambient conditions overnight. The CTAB and CCC were removed by solvent extraction. 0.5 g of as-synthesized sample was added into a mixture of EtOH (50 g) and HCl (2 g). The extraction was carried out under reflux condition (333 K for 24 h) and repeated for several times until the complete removal of the templates.

In the synthesis of CSBA-15, Pluronic P123 (1.2 g), CTAB (0.2 g) and CCC (0.03 g) were dissolved in 30 g of deionized water. EtOH (6 g) and HCl (37%, 1 g) were added into the above-mentioned aqueous solution and stirred at 313 K for 1 h. TEOS (3.7 g) was added to the mixture drop-wise and aged at 353 K for 2 h under refluxing condition. The molar composition of the synthesis mixture was 1 (SiO₂): 0.01 (P123): 0.03 (CTAB): 0.01 (CCC): 7.6 (EtOH): 0.5 (HCl): 92 (H₂O). The products were recovered by filtration and dried under ambient conditions overnight. P123, CTAB and CCC were completely removed by solvent extraction as specified previously.

To synthesize CSBA-16, Pluronic F127 (0.5 g), CTAB (0.11 g) and CCC (0.0166 g) were dissolved in 30 g of 2 M HCl solution. TEOS (2 g) was added to the mixture drop-wise and aged at 298 K for 24 h. The mixture was transferred to an autoclave and kept static at 373 K for 24 h. The molar composition of the synthesis mixture was 1 (SiO₂): 0.004 (F127): 0.03 (CTAB): 0.01 (CCC): 6.4 (HCl): 160 (H₂O). The products were recovered by filtration and dried under ambient conditions overnight. F127, CTAB and CCC were completely removed by solvent extraction as specified previously. The corresponding ACMS, including MCM-41, SBA-15 and SBA-16,

were synthesized following the same procedures described above in the absence of CCC.

3.2.5 Optimization of CMCM-41 synthesis

To investigate the influence of variations in preparation parameters on the properties of final CMCM-41 products and understand the mechanism of chirality transfer, CCC/Na₂SiO₃ ratio, EA/Na₂SiO₃ ratio and the amount of KCl added were screened based on the synthesis approach mentioned above. In a refined synthesis of CMCM-41, CTAB (0.133 g) and CCC (0.078 g) were dissolved in deionized water (40 g) and stirred at 313 K for 1 h. Na₂SiO₃ (0.12 g) was added to the mixture and stirred until a clear solution was obtained. EA (0.53 g) was added to the above solution under vigorous stirring. The mixed chemicals was allowed to react at room temperature under static condition for 6 h, and aged in a sealed beaker at 313 K for another 8 h. The products were recovered by centrifugal separation and dried under ambient conditions overnight. The surfactants and cobalt complexes were completely removed by solvent extraction.

3.2.6 Loading Pt nanoparticles onto CMCM-41 by using MAPR method

To deposit Pt nanoparticles onto CMCM-41 support materials, 0.04 g CMCM-41 was immersed in H₂PtCl₆·6H₂O aqueous solution and dried at 333 K in vacuum. 20 mL of EG was added to the above-mentioned Pt/CMCM-41 composite followed by sonicating for 10 min to afford a homogenous suspension. The said suspension was transferred into a three-neck flask with a condenser and placed in a microwave reactor (Sineo, MAS-II). The slurry was agitated by a magnetic stirrer and the temperature inside the flask was monitored by an infrared sensor. The suspension was heated to

438 K in 0.5 min and kept at the same temperature for 1.5 min. After cooling to the room temperature, the powder was filtrated out and washed with deionized water followed by drying at 333 K in vacuum and storing under ambient conditions.

3.2.7 Synthesis of monodentate phosphoramidite ligand (MPL)

(S)-(1,1'-Binaphthalene-2,2'-dioxy)chlorophosphine (BPC) was prepared prior to the synthesis of MPL. Under argon protected atmosphere, a solution of BINOL (0.86 g) in THF (25 mL) was added into a pre-cooled (273 K) mixture of PCl_3 (270 μL), triethylamine (860 μL) and THF (5 mL). After stirring for 4 h, the synthesis mixture was heated to room temperature and stirred at room temperature for another 12 h. The slurry was filtered under argon atmosphere. The clear filtrate was dried under vacuum, which afforded the light yellow color foams (BPC).

In the synthesis of MPL, the prepared BPC was dissolved in 15 mL of dried THF and injected into a pre-cooled (273 K) solution of N-ethylaniline (0.35 g) in the mixture of THF (10 mL) and triethylamine (2 mL). After stirring for 48 h at ambient temperature, the reaction mixture was filtered over celite under argon. Chromatography was performed by using a mixture of dried hexane and dichloromethane (1:1) as effluent over dried silica gel under argon. The final product was denoted as BPEAn.

3.2.8 Immobilization of MPL-based Rh catalysts on substrate surfaces

Immobilization of MPL-based Rh chiral catalysts on silica support surfaces (represented by SBA-15 molecular sieves) was carried out by a four-step modification method. To introduce amine functional groups onto SBA-15 surfaces, 0.5 g of pre-dried SBA-15 (373 K in vacuum overnight) was dispersed in 15 g of toluene and the

mixture was refluxed at 383 K under argon for 4 h, then 0.5 g of AnPTMS was added and the mixture was kept refluxing at 383 K for another 4 h. The powders (An-SBA-15) were filtrated out and washed with 2-propanol and CH_2Cl_2 alternatively. The residue hydroxyl groups on An-SBA-15 may react with BPC, and thus have to be removed completely. An extremely active silane—MSiN agent which can easily react with silanol groups [15] was selected for the further surface modification before introducing BPC. 0.15 g of dried An-SBA-15 (343 K in vacuum overnight) was dispersed in 10 g of toluene and the mixture was refluxed at 383 K for 4 h under argon, cooled to room temperature. 0.032 g (0.2 mmol) of MSiN was added to the mixture and stirred at room temperature for 14 h, 1 h at 333 K and 0.5 h at 343 K. The powders (M-An-SBA-15) was filtrated out, washed with toluene repeatedly and dried under vacuum. The functionalized SBA-15 powder was immersed in pre-cooled (273 K) solution of BPC (0.3 g) dissolved in the mixture of THF (30 mL) and triethylamine (2 mL). The slurry was stirred at 273 K for 8 h, following by stirring at room temperature for another 48 h. The solid was filtered out and washed using 120 mL of dried THF under argon atmosphere. The final powder binding with integrated ligands was denoted as BPEAn-SBA-15. Immobilized catalysts were prepared by introducing $\text{Rh}(\text{COD})_2\text{BF}_4$ with or without free MPL in CH_2Cl_2 .

3.3 Catalytic reactions

3.3.1 Selective hydrogenation of CALD

Selective hydrogenation of CALD was carried out in a stainless steel reactor with Teflon liner (Parr 4950, controller 4843). A certain amount of catalyst (0.01 g), 0.2 g of CALD (1.5 mmol) and 7.25 mL of solvent were added into the reactor. Tetradecane

(38 μ L, 0.146 mmol) was added as an internal standard. The air residue inside the reactor was expelled by pressurizing and releasing hydrogen several times. The reaction was performed at 333 K under 10 atm of hydrogen for either 1 or 0.5 h depending on the catalyst activity. In order to eliminate the external mass transfer limitation, the effect of stirring speed on CALD conversion was studied. The results show that CALD conversion is constant when the stirring speed is above 600 rpm, denoting a kinetics controlled regime (see Figure 3.5). Thus, the stirring speed was set at 600 rpm for all the experiments in this study. After the reaction, the catalyst powder was filtered off and the filtrate was analyzed using a gas chromatograph (Agilent, 6890N) equipped with a HP-5 column (Agilent) and FID. The by-products were identified by gas chromatography-mass spectrometry (GC-MS, Agilent, GC 6890N, MS 5973 inert).

Figure 3.5 Effect of external mass transfer on conversion of CALD over Pt/CNT-973 at 333 K under 10 atm of hydrogen for 1 h by using 2-propanol as solvent.

3.3.2 Enantioselective hydrogenation of dimethyl itaconate

Enantioselective hydrogenation of dimethyl itaconate was carried out in a stainless steel reactor with Teflon liner (Parr 4950, controller 4843). 0.005 g of Pt/CMCM-41 catalyst, 0.05 g of dimethyl itaconate and 5 mL of CH₂Cl₂ were added into the reactor. The reaction was run for 24 h at various temperatures and pressures. After the reaction, the catalyst powder was filtered off and the filtrate was analyzed using a gas chromatograph (Agilent, 6890N) equipped with a chiral column Chiraldex G-TA (30m × 250μm × 0.125μm) and a FID. The enantio-excess (*ee*, %) of products was calculated by using the following equation:

$$ee = (R-S) \times 100\% / (R+S) \quad (3.4)$$

where R and S represent the peak areas of GC signals for R and S enantiomers of hydrogenation products, respectively.

For homogeneous catalyst composed by BPEAn and Rh, 0.0017g (4 μmol) or 0.0034 g of BPEAn was mixed with 0.0016 g of Rh(COD)₂BF₄ in CH₂Cl₂ solution (4 mL) to afford a ligand/metal ratio equal to 1:1 (BPEAn-Rh) or 2:1 (BPEAn×2-Rh), respectively. 0.0316 g of dimethyl itaconate was added and the hydrogenation reaction was conducted at 298 K under 5 bar for 16 h. For BPEAn-based Rh catalyst immobilized on SBA-15, 0.0318 g of PMAAn-SBA-15 (0.9 wt.% of phosphorous determined by ICP measurement, and thus the immobilized ligands on 0.0318 g of PMAAn-SBA-15 is 4 μmol) and equal numbers of mole of Rh(COD)₂BF₄ (0.0016g) was stirred in CH₂Cl₂ solution (4 mL) for 5 h at 298 K, followed by washing with 6 mL of CH₂Cl₂ to afford the ligand/metal ratio of 1:1 (BPEAn-Rh/SBA-15). The heterogeneous catalyst with ligand/metal ratio of 2:1 (BPEAn×2-Rh/SBA-15) was

prepared by adding 0.0017 g of free MPL—BPEAn to BPEAn-Rh/SBA-15, the mixture was immersed in 4 mL of CH_2Cl_2 and stirred for 5 h at 298 K. The catalyst was filtrated out and washed with 6 mL of CH_2Cl_2 . Homogeneous catalysts composed by BPEAn and Rh with different ligand/metal ratio (1:1 and 2:1) were also immobilized on CNTs via adsorption method. CNTs was annealed at 973 K for 2 h under nitrogen flow (40 mL/min) to remove the oxygen-containing groups from the surface. For CNTs supported catalyst with ligand/metal ratio = 1 (BPEAn-Rh/CNTs), BPEAn (0.0017 g) and CNTs (0.1 g) were mixed in CH_2Cl_2 and stirred at 298 K for 4 h. Subsequently, $\text{Rh}(\text{COD})_2\text{BF}_4$ (0.0016g) was added and kept stirring for another 12 h. The heterogenized catalysts were obtained by evaporating CH_2Cl_2 under vacuum. CNTs supported catalyst with ligand/metal ratio = 2 (BPEAn $\times$ 2-Rh/CNTs) was prepared by re-dispersing BPEAn-Rh/CNTs in the CH_2Cl_2 solution of BPEAn (0.0017 g), the slurry was stirred for 12 h at 298 K and then dried under vacuum. The hydrogenation reaction conditions were the same with those adopted for the generation of BPEAn based homogeneous catalyst. Recycle of heterogeneous catalysts was conducted by filtrating the catalyst powder from reaction mixture and washing with 10 mL CH_2Cl_2 for several times.

List of abbreviations

ACMS	Achiral Mesoporous Silica
AnPTMS	N-[3-(Trimethoxysilyl)-propyl]aniline
BET	Brunauer-Emmett-Teller
BINOL	S-(-)-1,1'-Bi(2-naphthol)
BJH	Barrett-Joyner-Halenda
BPC	(S)-(1,1'-Binaphthalene-2,2'-dioxy)chlorophosphine
CALD	Cinnamaldehyde
CCC	Chiral Cobalt Complex
CD	Circular Dichroism
CMS	Chiral Mesoporous Silica
CNTs	Multi-Walled Carbon Nanotubes
CO Stripping	Carbon Monoxide Stripping
CTAB	Hexadecyltrimethylammonium Bromide
CV	Cyclic Voltammetry
DACH	(±)- <i>trans</i> -1,2-Diaminocyclohexane
DLS	Dynamic Light Scattering
EA	Ethyl Acetate
EAS	Electrochemical Active Surface
<i>ee</i>	Enantio-Excess
EG	Ethylene Glycol
EPR	Electron Paramagnetic Resonance
EtOH	Ethanol

F127	EO ₁₀₆ PO ₇₀ EO ₁₀₆
FID	Flame Ionization Detector
FTIR	Fourier Transform Infrared Spectroscopy
GC-MS	Chromatography-Mass Spectrometry
H ₂ -TPR	Hydrogen Temperature Programmed Reduction
ICP	Inductively Coupled Plasma
IMP	Impregnation
LCP Radiation	Left Circularly Polarized Radiation
MAPR	Microwave-Assisted Polyol Reduction
MPL	Monodentate Phosphoramidite Ligand
MSiN	Hexamethyldisilazane
NEt ₃	Triethylamine
NMR	Nuclear Magnetic Resonance
P123	EO ₂₀ PO ₇₀ EO ₂₀
PCl ₃	Phosphorous Trichloride
RCP Radiation	Right Circularly Polarized Radiation
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscopy
TEOS	Tetraethyl Orthosilicate
THF	Tetrahydrofuran
UV	Ultraviolet
UV-vis	UV-visible
VCD	Vibrational Circular Dichroism

XANES

X-ray Absorption Near Edge Structure

XPS

X-ray Photoelectron Spectroscopy

XRD

X-Rays Diffraction

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Chapter 4 Carbon Nanotube Supported Pt-based Bimetallic Catalysts Prepared by a Microwave-Assisted Polyol Reduction Method and Their Catalytic Applications in the Selective Hydrogenation of Cinnamaldehyde to Cinnamal alcohol

Selective hydrogenation of unsaturated carbonyl compounds is of paramount importance in pharmaceutical and fragrance industries [1]. Selective hydrogenation of cinnamaldehyde (CALD) to cinnamal alcohol (CALC) is a representative example of such reactions. [2]. Recent studies have focused on the effects of supports and promoters on the activity and selectivity of Pt metallic nanoparticles in CALD selective hydrogenation. Different support materials may lead to distinctive hydrogenation results due to the specific interactions between support and Pt nanoparticles [3]. The catalytic performance of metallic nanoparticles may also be drastically changed by modifying the surface chemistry of the support, e.g., the activity of Pt nanoparticles was enhanced by a factor of 25 after removing the surface oxygen-containing groups from a carbon nano-fiber (CNF) support [4]. Another promising approach to enhance the catalytic properties of Pt nanoparticles is to introduce a second metal (or metal oxide) to form bimetallic catalysts. It has been reported that metal promoters, such as Ga [4], Co [5], Ru [6], play a vital role in CALD hydrogenation in the presence of supported Pt nanoparticles due to the synergetic interactions between Pt active sites and promoters.

In addition to support and promoter, other factors, e.g., the preparation method, may also affect the outcome of selective hydrogenation. Several methodologies have been developed to synthesize Pt-based bimetallic catalysts. Although the procedures of

ion-exchange and impregnation (IMP) methods are simple, the activities of as-synthesized catalysts are usually poorer as compared to the catalysts prepared by more sophisticated approaches, such as homogeneous deposition precipitation (HDP) and reductive deposition precipitation (RDP) [4]. The successive reduction steps in RDP result in close contact between promoters and main active centers, which affords favorable catalytic properties in selective hydrogenation [4]. Recently, a novel preparation method, i.e., microwave-assisted polyol reduction (denoted as MAPR) technique has been proposed to synthesize Pt-based electro-catalysts for fuel cells [7, 8]. Microwave irradiation allows uniform heating of the metal precursors to a high temperature within a few seconds, leading to a shorter crystallization time and more homogenous nucleation as compared to conventional preparation methods [8].

In this chapter, we apply this facile MAPR method to prepare Pt-based bimetallic catalysts with high activity and selectivity for CALD hydrogenation, superior to those catalysts synthesized by the conventional IMP method. The effects on the catalytic performance of as-prepared bimetallic catalysts due to the pretreatment of multi-walled carbon nanotube (CNTs) support surfaces, solvents and transition metal (metal oxide) promoters are examined. It is revealed that different from IMP method, MAPR retains the hydrophobic surface properties of CNTs, affords close contact between promoters and Pt nanoparticles, e.g., metal-metal electronic interaction, which significantly improves the catalytic performance of Pt active sites. Interestingly, other than generally adopted solvents such as alcohols [1, 2] and alkanes [9], the as-prepared catalysts in this study showed remarkably high activity and selectivity in the presence of ethyl acetate (EA) as the solvent. Hammersley sequence sampling (HSS)

method was employed to optimize the metal loadings in this catalytic system involving Pt active sites and two promoter metals.

4.1 Effects of CNTs surface oxygen-containing groups

Catalyst support may influence hydrogenation via steric or electronic interaction, which is usually contributed by the surface properties of support material [10]. The surface oxygen-containing groups on a carbonaceous support including carboxylic, carbonyl and hydroxyl moieties are initially indispensable to enhance the loading and dispersion of metal precursors [8]. Interestingly, removal of these oxygen-containing groups from CNF [11] surfaces by a high-temperature treatment after loading metal particles remarkably increases both selectivity and activity in hydrogenation. Toebe et al. reported the correlation between the surface oxygen density and the performance of CALD hydrogenation over a CNF supported Pt catalyst [12]. They suggested that the oxygen-containing groups could be effectively removed from carbonaceous surfaces when the annealing temperature was higher than 573 K. Herein, the effects of CNTs surface oxygen-containing groups on hydrogenation performances over the catalysts prepared by MAPR were examined. Pt/CNT catalysts were pretreated in a temperature range from 673 to 973 K in nitrogen.

Various techniques, involving XPS, Boehm titration, thermogravimetric analysis (TGA) and chemical derivatization have been employed to characterize the functional groups bonded on CNF [12] and CNTs [13] surfaces. In this study, the density of surface oxygen-containing groups on CNTs was related to their electrochemical properties.

Figure 4.1 (a) Cyclic voltammograms (CVs) of Pt/CNT catalysts treated with different temperature treatments in 1 M KOH solution with a scan rate of 50 mVs^{-1} ; (b) Magnification of the circled area in (a) showing shift of Pt-O reduction peaks.

CV measurements were conducted on Pt/CNT catalysts and the results are shown in Figure 4.1a. As the pretreatment temperature increases, a remarkable decrease of the area enclosed by CV curves, i.e., the background of CV signal is observed. Similar result is also obtained for pure CNTs before and after high temperature annealing in inert atmosphere (see Figure 4.2). The decrease of area enclosed by CV curves has been reported by Lawrence et al. [14]. In their study, CV profiles of CNTs prepared by different methods (including arc discharge and chemical vapor deposition) were assessed, and they suggested that a larger quantity of redox active sites (e.g., quinone) on CNTs surfaces led to a larger capacitance and CV background. A similar trend was

also observed on the carbon black pretreated in HNO_3 with different concentrations and pretreatment time durations [15]. Boiling carbon black in a concentrated HNO_3 solution for 18 h resulted in the elimination of surface oxygen-containing groups (such as quinone and hydroquinone), and consequently a small area enclosed by the CV curves. Therefore, the decrease of CV background upon high-temperature annealing observed in this study suggests the removal of oxygen-containing groups from CNTs surfaces.

Figure 4.2 CV curves of the CNTs supports before (CNTs) and after high temperature annealing (CNT-973).

In these CV profiles, redox peak signals at *ca.* -0.7 and -0.5 V are contributed by the adsorption and desorption of hydrogen atoms bonded on Pt surface [16]. These peaks become less pronounced at higher annealing temperatures, implying the decrease in Pt surfaces areas, i.e., enlargement of the Pt particle sizes. Due to the low

Pt loading, the platinum oxide (Pt-O) reduction peaks [17] are only discernable for Pt/CNT-773, Pt/CNT-873 and Pt/CNT-973 with low backgrounds as shown in Figure 4.1b which is the magnification of circled area in Figure 4.1a. The reduction potential depends on the thermodynamics of metal oxide, kinetics of all involved reduction steps and the electrochemical environment [18]. In an alkaline solution, Pt-O reduction follows the steps [16]:

The Pt-O reduction potential decreases with increasing pretreatment temperature, implying that low density of surface oxygen-containing groups hampers the Pt-O reduction. Removal of surface oxygen increases the hydrophobicity of CNTs surfaces, which hinders the contact of water with CNTs support, resulting in a slow Pt-O reduction. Although a low density of surface oxygen-containing groups leads to a high conductivity of CNTs [6], which may enhance the current flow in response to the applied potential (i.e., accelerate the diffusion of electrons to Pt particles) and result in a positive shift of the Pt-O reduction potential, the water accessibility to CNTs, i.e., the hydrophobicity of support material plays a more important role in this particular reduction step.

CO stripping voltammetry is measured to characterize the catalysts with and without high-temperature pretreatment. In CO stripping, CO initially adsorbed on Pt nanoparticles will be oxidized to CO₂ at a negative potential along with the positively sweeping potential of the working electrode. The potential for CO oxidization relies on the electrochemical properties and chemical environment of Pt nanoparticles. In

addition, compared to CV measurement, CO stripping is a more feasible method to determine the electrochemical active surface (EAS) areas of Pt nanoparticles when Pt loading is low, due to the low electrical signals attributed to the desorption of hydrogen atoms bonded on Pt surfaces and the uncertainty introduced by the background current subtraction [19]. Figure 4.3 shows the CO stripping voltammograms of catalysts pretreated under different temperatures. The main peak potential for CO oxidization remains constant for all the catalysts, whereas the onset potential, at which CO stripping current attains 10% of the current at main peak potential [19], negatively shifts when the pretreatment temperature increases, suggesting that CO is more easily oxidized on catalyst surfaces with fewer oxygen-containing groups. It was reported that the oxidization of CO adsorbed on Pt-Ru nanoparticles supported on pristine CNTs was easier as compared to the case of having the Pt-Ru nanoparticles supported on partially oxidized CNTs, and the promoted CO elimination was assisted by the high conductivity of pristine CNTs [20]. Vu et al. reported that the conductivity of a pristine CNTs pellet is 1.5 times higher than that of CNTs pretreated with HNO₃ [6]. Thus, the negative shift of CO oxidization peak is contributed by the improved conductivity of CNTs after removing the surface oxygen-containing groups. The EAS areas of Pt nanoparticles were calculated based on the CO stripping voltammetry (see Chapter 3 Equation 3.2), assuming that the oxidation of a CO monolayer adsorbed on 1 cm² of Pt requires 0.484 mC. The results show that the CO active surface areas of Pt sites decrease (see Table 4.1), implying the sintering of small Pt nanoparticles at high temperatures. These observations were further evidenced by XRD and TEM measurements.

Figure 4.3 CO stripping voltammograms of Pt/CNT catalysts treated with different temperatures. The left and right dash lines indicate the onset and peak potentials of Pt/CNT, respectively.

Figure 4.4a shows the XRD patterns of Pt/CNT catalysts pretreated in a nitrogen flow at different temperatures. The strong (002) diffraction of hexagonal graphite at 2θ of 25.8° suggests that the graphite structure of CNTs is retained after oxidizing CNTs in HNO_3 , depositing Pt precursors under microwave irradiation and subsequently pretreating at high temperatures [21]. The diffraction peaks at 2θ of 39.7° , 46.2° and 67.4° are attributed to the cubic platinum metal structure [22]. The

average diameters of Pt nanoparticles (calculated based on the full width at half maximum of Pt (111) reflection using Scherrer's equation [21]) increase from 3 to 5 nm upon the high-temperature pretreatment, as listed in Table 4.1.

Figure 4.4 (a) XRD patterns of Pt/CNT treated with different temperatures; (b) XRD patterns of PtFe/CNT-973, PtCo/CNT-973, Pt/CNT-973, PtFe/CNT-973-IMP and PtCo/CNT-973-IMP.

CO stripping and XRD results are in good agreement with those of direct TEM observations on Pt/CNT and Pt/CNT-973 as shown in Figure 4.5a and b. Pt/CNT shows a mean particle size at around 3.7 nm with a narrow size distribution. A noticeable particle size increment is observed and the particle size distribution is substantially wider after pretreating Pt/CNT at 973 K. The aggregation of Pt nanoparticles caused by the high-temperature pretreatment in this study is more noticeable than that of the carbon supported Pt nanoparticles prepared by either IMP

or HDP method [6, 12]. For MAPR, Pt is reduced in the liquid phase, the nucleation and growth of Pt nanoparticles may take place either in the EG solution or on the CNTs surfaces. Although the latter case is preferable due to the ionic interaction between CNTs surface groups and Pt precursors [23], it is still arbitrary to preclude the possibility that Pt particles initially form in EG followed by adsorbing onto CNTs surfaces, as nano-sized noble metal particles can be formed in EG solutions in the absence of any support [7]. Meanwhile, the nucleation and growth of Pt nanoparticles occur primarily on CNTs surface for IMP or HDP approach. It was reported that CNTs-supported metal nanoparticles can catalyze the localized gasification of carbon when the sample was pretreated at a high temperature, giving rise to the formation of nano-scaled ridges and cavities (docking stations) on CNTs surfaces, which may play an anchoring role in facilitating the immobilization of metal nanoparticles [24]. Therefore, the mobility of Pt nanoparticles on CNTs surfaces prepared by MAPR is higher than that of CNTs-supported Pt nanoparticles synthesized by IMP or HDP, resulting in a remarkable increase of the Pt nanoparticle size under a high-temperature pretreatment. Nevertheless, an optimized utilization of Pt active sites may be achieved under such circumstances because the interaction between support and Pt nanoparticles is minimized to a large extent [25, 26].

Figure 4.5 TEM images and particle size distributions of (a) Pt/CNT, (b) Pt/CNT-973, (c) Recycled Pt/CNT-973 after hydrogenation of CALD in 2-propanol at 333K under 10 atm of hydrogen for 1 h; (d) PtFe/CNT-973, (e) PtCo/CNT-973, (f) PtFe/CNT-973-IMP and (g) PtCo/CNT-973-IMP, respectively.

To compare the catalytic properties of Pt/CNT pretreated at different temperatures, selective hydrogenation of CALD was conducted in 2-propanol (a commonly used solvent) and the results are listed in Table 4.1. For Pt/CNT pretreated at relatively low temperatures (673 and 773 K), CALD conversion dramatically decreases as compared to the pristine Pt/CNT, which may be attributed to the increased Pt particle size, i.e., diminishing of the available Pt active sites evidenced by EAS area measurements. Further increasing the annealing temperature leads to the elevation of conversion though the Pt particle size slightly increases. The CNTs surface with a low oxygen density is beneficial for the π - π interaction between aryl ring of CALD and the basic π sites on CNTs surfaces [6]. Therefore, the local concentration of CALD on CNTs surfaces increases, resulting in an enhanced catalytic activity (as shown in Scheme 4.1a). The turnover frequency (TOF, calculated based on EAS areas) monotonically increases with the pretreatment temperature, suggesting the beneficial effect of removing surface oxygen from CNTs support. TEM image shows that the Pt nanoparticle sizes remain essentially constant after the hydrogenation reaction (see Figure 4.5c).

Scheme 4.1 (a) Hydrogenation of CALD on oxygen-containing CNTs (left) and oxygen-free CNTs (right) supported catalysts; (b) Two hydrogenation pathways in EA; (c) Hydrogenation of CALD on bimetallic catalysts synthesized using IMP (left) or MAPR (right) methods.

The effect of pretreatment temperature on selectivities is also distinct. When the catalysts supported on CNTs with relatively high densities of surface oxygen-containing groups (Pt/CNT, Pt/CNT-673 and Pt/CNT-773) are tested, the product distributions are dominated by undesired compounds which are not derived from CALD hydrogenation but from side reactions, such as aldol condensation, oxidation and esterification [2, 12]. These by-products have been identified using GC-MS and listed in the footnotes of Table 4.1. Toebe et al. suggested that these side reactions were acid-catalyzed; removing oxygen-containing groups from CNTs surfaces decreased the acidity of CNTs surfaces, which suppressed the formation of these by-products [12]. Unlike IMP and HDP preparation methods, in which the surface oxygen-containing groups on carbon supports may be partially removed after pre-reducing the catalyst in H₂ at a high temperature, the catalysts prepared by MAPR method were reduced in the liquid phase at a relatively low temperature. Therefore, compared to the catalyst prepared by IMP method, more oxygen-containing groups remain on CNTs surfaces (evidenced by CV measurements of monometallic Pt/CNT and the corresponding impregnated catalyst Pt/CNT-IMP, as shown in Figure 4.6), which may seriously impede the hydrogenation steps due to the acid sites on the CNTs support surfaces.

Table 4.1 Hydrogenation results of CALD over Pt/CNT with different temperature treatments by using 2-propanol as solvent.

Catalysts	Particle size ^a	EAS ^b	Conversion	Yield of products (mol %)				TOF ^d
	(nm)	(m ² g ⁻¹)	(%)	CALC	HALD	HALC	Others ^c	(h ⁻¹)
Pt/CNT	3.1 (3.7)	54.0	62.7	0	2.4	0	97.6	1213
Pt/CNT-673	4.5 (4.6)	31.0	37.2	0	5.2	0	94.8	1253
Pt/CNT-773	4.9 (4.8)	29.4	38.6	0	7.6	0	92.4	1371
Pt/CNT-873	5.2 (5.2)	22.6	53.5	43.5	7.1	0	49.4	2473
Pt/CNT-973	5.1 (5.4)	23.0	49.6	55.1	4.6	0	40.3	2288

^a particle sizes were calculated from XRD patterns of Pt based on Scherrer's equation (outside the parenthesis) as well as from TEM measurements (inside the parenthesis);

^b EAS areas were deduced from data of CO stripping;

^c Based on the characterization of GC-MS the other by-products include 1-(3-propoxyprop-1-enyl)benzene, cinnamyl formate, cinnamic acid, benzyl cinnamate, 4,4-diphenylcyclohexa-1,5-dienyl acetate and some condensation products which can not be identified by our GC-MS due to their large molecular weights;

^d TOF is defined as the number of converted CALD molecules in 1 h over one active site, the number of active sites (Pt atoms exposed on the surface of particles) is determined by EAS value. Reaction time is 1 h.

Figure 4.6 CV curves of the CNTs supported Pt catalysts prepared by MAPR (Pt/CNT) and IMP (Pt/CNT-IMP) methods.

Kinetic studies of CALD hydrogenation were conducted and the results are shown in Figure 4.7. At the initial stage of reaction (within 5 min), Pt/CNT-973 outperforms Pt/CNT-773, regardless of the similar amount of by-products formed over both catalysts. The superior activity of Pt/CNT-973 can be attributed to the removal of oxygen-containing groups from CNTs surfaces, which enhances the π - π interaction between CALD and CNTs. Nevertheless, the reaction rate over Pt/CNT-973 decreases gradually, which may be due to deactivation of catalytic sites caused by the deposition of carbonaceous by-products. The formation of carbonaceous deposits in the liquid catalytic system is referred as fouling which has been extensively investigated by Hajek et al. [27, 28]. In a low-temperature reaction, the transformation of hydrocarbons does not occur and the carbonaceous deposits are mostly non-desorbed

[28]. However, further formation of by-products is inhibited to a large extent as a result of the hydrogenation steps and the rapid decrease of CALD concentration, as shown in Figure 4.7. In the case of Pt/CNT-773, constantly producing a large amount of by-products caused by the acid sites on CNTs surfaces may exacerbate the catalyst deactivation. These results reveal that side reactions dominate the conversion of CALD over Pt/CNT-773, while the competition between hydrogenation and side reactions is observed over Pt/CNT-973.

Figure 4.7 Kinetic studies on hydrogenation of CALD over Pt/CNT-773 and Pt/CNT-973 by using either 2-propanol or EA as a solvent. (a) Conversion of CALD as a function of time; (b) Percentage of CALD converted to by-products as a function of time.

Reasonable selectivity towards hydrogenation is obtained over Pt/CNT-873 and Pt/CNT-973; and the major hydrogenation product is CALC. These results further

suggest that elimination of surface oxygen from CNTs can facilitate the hydrogenation steps, especially the hydrogenation of C=O bond. Vu et al. suggested that the conductivity of CNTs was improved by removing electronegative oxygen atoms from the CNTs surface [6], which was further proved by the negatively shifted onset potential for CO oxidation in this study. The increased conductivity of CNTs may enhance the electron transfer from CNTs to metal active sites [6]. The enriched electron density surrounding the metallic nanoparticles reduces the probability of C=C bond coordinated to Pt active sites due to the electronic repulsion, thereby increases the selectivity towards CALC [6]. It is worth mentioning that the product distribution is different from the reported results over the Pt nanoparticles supported on CNF, in which the CALC selectivity decreased with the density of surface oxygen-containing groups on CNF, although both activity and selectivity towards total hydrogenation product were improved [12]. The Pt nanoparticle size for Pt/CNT-973 (5 nm) is larger than that of the catalyst reported by Toebe et al. (1-3 nm) [12], and it has been generally accepted that a slightly larger Pt nanoparticle size leads to a higher selectivity towards CALC due to the steric effect [10, 11]. Furthermore, the curved graphite surface of CNTs is beneficial to the charge transfer as compared to other carbon structures [29]. CNF is of a fishbone type structure with the edges of graphite planes exposed at the surface [12], the enhancement of electron transfer by removing surface oxygen is less pronounced for CNF due to the orientation of graphite layers and the hydrogen atoms at the external edges.

4.2 Effects of hydrogenation parameters

Compared to the large number of reports on designing effective catalysts, investigations of the solvent effect on CALD hydrogenation are limited [10]. The solvent plays a crucial role in this particular hydrogenation reaction: some solvents such as alcohols may be involved in the side reactions [12] and hydrocarbon solvents usually give a poor activity [10]. In this study, six solvents were examined for CALD hydrogenation over Pt/CNT-973 and the results are listed in Table 4.2. The hydrogenation activities and selectivities show a strong dependence on the selection of solvent. It was suggested that a polar solvent enhances the formation of products that are more polar than reactants [30]. The polarities of solvents in this study are of the following sequence: cyclohexane < 1-butanol < 2-propanol < EA < dioxane < ethanol. Regardless two special solvents (EA and dioxane), both activity and selectivity towards CALC increase with solvent polarity due to the higher polarity of CALC than that of CALD [31]. No reaction took place in dioxane under the current hydrogenation conditions, implying that the catalyst may be poisoned by dioxane due to the solvent adsorption. A similar result was reported in a previous work: dioxane was strongly adsorbed on Ru surfaces, which was attributed to the interaction between surface noble metal atoms and the unshared electron pair donated by oxygen atoms of dioxane [32]. It was also suggested that Pt-based catalysts interacted more strongly with solvent than Ru-based catalysts [32]. Significant improvements in catalytic activity and selectivity were obtained when using EA as the solvent. EA out-performs other solvents and the TOF increases by a factor of 4 and 2 as compared to two commonly used solvents cyclohexane and 2-propanol, respectively.

Table 4.2 Hydrogenation results of CALD over Pt/CNT-973 in different solvents.

Solvents	Polarity of solvents	Conversion (%)	Yield of products (mol %)				TOF ^b (h ⁻¹)
			CALC	HALD	HALC	Others ^a	
Cyclohexane	0.2	23.4	17.7	16.9	0	65.4	1062
1-Butanol	4.0	39.0	34.0	6.6	0	59.4	1771
2-Propanol	4.3	49.6	55.1	4.6	0	40.3	2288
Ethyl acetate	4.4	89.8	78.8	6.8	14.2	0.2	4079
1,4-Dioxane	4.8	0	--	--	--	--	--
Ethanol	5.2	64.9	47.6	5.2	0	47.2	2948

^a Based on the characterization by GC-MS, the other by-products include 1-(3-propoxyprop-1-enyl)benzene, 1-((E)-3-propoxyprop-1-enyl)benzene, 1-(3-ethoxyhexa-1,5-dienyl)benzene, cinnamyl formate, cinnamic acid, benzyl cinnamate, 4,4-diphenylcyclohexa-1,5-dienyl acetate, 2-(hydroxy(phenyl)methyl)hexanal and some condensation products which can not be identified by our MS due to their large molecular weights.

^b TOF is defined as the number of converted CALD molecules in 1 h over one active site, the number of active sites (Pt atoms exposed on the surface of particles) is determined by EAS value. Reaction time is 1 h

Solubility of hydrogen in the solvent may play a significant role in this catalytic reaction. The hydrogen solubility in EA is higher than any other alcohol employed in this study [33], which may partially contribute to the improved activity in EA. Although the hydrogen solubility in alcohols is proportional to the molecular weight of alcohols [33], a poor catalytic activity of hydrogenation is observed in 1-butanol, which may be due to the low polarity of 1-butanol and the catalyst deactivation derived from the high selectivities towards by-products. High pressure increases the solubility of hydrogen in EA [33]. In this study, CALD hydrogenation in EA under different hydrogen pressures shows that high pressure leads to a high conversion along with an improved selectivity towards HALC rather than CALC (see Table 4.3). On the other hand, hydrogenation of CALD in EA over bared CNTs after high temperature (973 K) annealing under the same reaction conditions (10 atm of hydrogen, 333 K for 1 h) shows a conversion of 6.0% and 100% selectivity towards HALD. Similar results (5.9% of CALD conversion and 100% of HALD selectivity) are obtained when the reaction is performed in the absence of any catalyst, implying the lack of catalytic capability of CNTs in this particular reaction. These results suggest that CALD hydrogenation in EA may undergo a distinct reaction pathway besides the direct hydrogenation of CALD by H atoms adsorbed on Pt nanoparticles.

Table 4.3 Hydrogenation results of CALD over Pt/CNT-973 under different hydrogen pressures in EA at 333 K, reaction time: 1 h.

Pressure (atm)	Conversion (%)	Yield of products (mol %)			
		CALC	HALD	HALC	Others ^a
5	71.5	81.0	8.8	10.0	0.2
10	89.8	78.8	6.8	14.2	0.2
15	98.4	64.5	4.0	31.4	0.1
20	99.8	40.4	1.4	58.0	0.2
30	100	23.9	0.8	75.2	0.1
40	100	19.2	0.5	80.1	0.2

^a Based on the characterization by GC-MS, the other by-products include cinnamyl formate, cinnamic acid, 4,4-diphenylcyclohexa-1,5-dienyl acetate and some condensation products which cannot be identified by our MS due to their large molecular weights.

Aiming at understanding the role of a solvent in the liquid phase reaction, the chemistry involving common organic solvents, e.g., esters, ethers and alcohols on Pt surfaces in the presence of H₂ has been investigated at room temperature using a reflection-absorption infrared spectroscopy (RAIRS) [34]. A small amount of CO adsorbed on Pt was detected due to the decomposition of ethanol. No CO adsorption was found when Pt was immersed in EA liquid film. As CO is notorious for its poison effect on Pt-based catalysts, the high stability of EA on Pt surfaces may partially explain why Pt/CNT-973 exhibits a remarkably high activity in EA. Investigations on EA hydrogenation revealed the formation of hemiacetal bonded on noble metal surfaces as an intermediate [35]. Herein, it is tentatively proposed that the hemiacetal

intermediate may also form and participate in the CALD hydrogenation. As illustrated in Scheme 4.1b, when EA adsorbs on Pt nanoparticle, dissociated hydrogen adsorbed on Pt transfers to the carbonyl group of EA. The oxygen of carbonyl group subsequently bonds to a vacant Pt site to form the hemiacetal intermediates [35]. Further reduction of EA is not preferable because it only occurs at a substantially higher temperature [35]. Hydrogen transfer may occur from the unstable hemiacetal intermediate to CALD, leading to the transfer hydrogenation between CALD and the intermediate. This proposed mechanism may explain why both selectivity and activity remarkably increase in EA. Firstly, the competitive adsorption of CALD and EA solvent on Pt surfaces is not necessary for hydrogenation because the intermediate can transfer hydrogen to CALD. This may be the major factor accounting for the high TOF in EA. Secondly, it is also not surprising to observe that the selectivities towards by-products contributed by side reactions are extremely low (0.2 %) due to the favorable hydrogenation of CALD in EA. The C=C double bond hydrogenation may also be suppressed due to the steric resistance between the intermediate and aryl ring of CALD, resulting in a high selectivity towards CALC. In contrast to the hydrogenation of CALD over Pt/CNT-973 in 2-propanol, detailed studies on the time-dependent catalytic behavior of Pt/CNT-973 in EA show that the CALD conversion is controlled by the hydrogenation steps (see Figure 4.7). By changing the solvent from 2-propanol to EA, the reaction rate remarkably increases, which can be attributed to the enhanced hydrogenation rates and suppressed formation of by-products. Thus, the possibility of depositing carbonaceous by-products on catalytic sites is minimized.

Table 4.4 Hydrogenation results of CALD over Pt/CNT-973 under 10 atm of hydrogen at 333 K in EA with different water contents, reaction time: 1 h.

Weight ratio of water (wt.%)	Conversion (%)	Yield of products (mol %)			
		CALC	HALD	HALC	Others
0.0 ^a	66.6	83.4	8.8	7.6	0.2
<0.2 ^b	89.8	78.8	6.8	14.2	0.2
0.2	76.3	82.6	7.9	9.3	0.2
0.4	73.2	82.4	8.9	8.6	0.1
0.8	63.0	84.9	10.7	4.3	0.1
1.6	51.2	84.4	10.9	4.6	0.1

^a The moisture-free EA was prepared by distillation of commercial EA over CaH₂;

^b Based on the catalogue of commercial EA.

As the commercial EA contains less than 0.2 wt.% of water, the influence of water content is also investigated by adding different amount of water in pre-dried EA (which is prepared by distillation of commercial EA on CaH₂). The results in Table 4.4 show that the activity over Pt/CNT-973 increases in the presence of a little amount of water in EA (<0.2 wt.%), followed by a rapid decrease due to the excess water content. Similar trend was also found in a ethanol-water system, in which the best result was obtained in the presence of 10 wt.% of water [36]. The remarkable difference is that even a trace amount of water (<0.2 wt.%) can influence the catalytic behavior dramatically in this study. Details of water effect are still under investigation.

4.3 Effects of promoters and preparation methods

Adding a second metal (or metal oxide) to a Pt-based catalyst as the promoter may influence the catalytic performance of this particular catalyst in CALD hydrogenation [10]. In this work, introducing the promoter was simply achieved by mixing Pt and promoter precursor solutions with CNTs support prior to the microwave-assisted reduction. Several transition metals were screened and the results are summarized in Table 4.5. Most of the promoters (Mn, Ni, Cu, Zn and Sn) show negative effects on CALD hydrogenation, whereas introducing Fe and Co improves CALC selectivity and CALD conversion, respectively. Fe and Co promoted Pt catalysts were also prepared by an IMP method and subsequently pretreated in nitrogen under a high temperature. As shown in Table 4.5, catalytic conversions dramatically decrease upon the impregnation of Fe and Co. The CALC selectivity remains constant for PtCo/CNT-973-IMP; and it decreases in the presence of impregnated Fe.

XRD patterns of these catalysts are shown in Figure 4.4b; diffraction peaks assigned to the cubic platinum metal structure are clearly discernable. No reflections from Fe or Co metallic and oxidized species can be detected due to the low Fe and Co contents (1.47 and 1.56 wt.% for Fe and Co, respectively). The broadening of diffraction peaks for PtCo/CNT-973-IMP suggests the formation of relatively small Pt particles. Pt particle sizes for these samples are listed in Table 4.5; no clear correlation between particle size and preparation method can be derived. The mean particle sizes and size distributions were further measured by TEM observations, as shown in Figure 4.5d, e, f and g. For the bimetallic catalysts synthesized by MAPR, the incorporation of Co affords a marginally larger Pt particle size and broader size distribution as

compared to the Pt particles promoted by Fe. Nevertheless, the trend inverses for the impregnated catalysts, small particles with a narrow size distribution are formed on the Co-modified catalyst. These results imply that the interaction between Pt and promoter may be different due to distinctive preparation strategies.

Table 4.5 Hydrogenation results of CALD over Pt based bimetallic catalysts in EA.

Catalysts	Particle size (nm)	EAS ($\text{m}^{-2} \text{g}^{-1}$)	Conversion (%)	Yield of products (mol %)				TOF ^a (h^{-1})
				CALC	HALD	HALC	Others	
Pt/CNT-973	5.1	23.0	59.8	80.9	12.8	6.2	0.1	5433
PtMn/CNT-973	4.5	--	45.6	71.6	28.0	0.2	0.2	--
PtFe/CNT-973	4.5	15.1	56.5	87.7	11.5	0.7	0.1	7818
PtCo/CNT-973	5.0	19.0	66.2	73.8	18.4	7.7	0.1	7280
PtNi/CNT-973	5.3	--	53.4	76.5	20.4	3.0	0.1	--
PtCu/CNT-973	5.1	--	38.1	59.5	40.4	0	0.1	--
PtZn/CNT-973	4.8	--	41.7	77.1	21.3	1.4	0.2	--
PtSn/CNT-973	5.2	--	20.0	50.1	49.8	0	0.1	--
PtFe/CNT-973-IMP	4.9	28.6	11.9	66.3	33.6	0	0.1	869
PtCo/CNT-973-IMP	3.6	35.7	17.4	80.4	19.5	0	0.1	1018

^a TOF is defined as the number of converted CALD molecules in 0.5 h over one active site, the number of active sites (Pt atoms exposed on the surface of particles) is determined by EAS value. Reaction time is 0.5 h.

Most of the promoter precursors are nitrate salts, and the promoters should be present in the form of oxides if they are located on Pt surface and exposed to air. The available surface areas of Pt particles (represented by EAS areas derived from CO stripping measurements) are summarized in Table 4.5. In general, the EAS area is inversely proportional to the particle size of Pt monometallic catalyst. The same trend also applies to PtFe/CNT-973-IMP and PtCo/CNT-973-IMP: both impregnated catalysts have smaller particle sizes and larger EAS areas than Pt/CNT-973. Although the particle sizes of PtCo/CNT-973 (5.0 nm) and PtFe/CNT-973 (4.5 nm) are smaller than that of Pt/CNT-973, the active surface areas of Pt for these two catalysts are also lower than that of Pt/CNT-973 (see Table 4.5). We suggest that the small surface area is contributed by the coverage of Fe or Co oxides on Pt nanoparticles, namely a close contact between promoters and catalytic active centers. The significantly high TOF suggests the superior activity of surface Pt atoms for PtFe/CNT-973 and PtCo/CNT-973, while the relatively poorer conversion for PtFe/CNT-973 is attributed to the lower EAS area, i.e., fewer exposed Pt surface atoms. These observations imply that C=O bond activation in CALD hydrogenation is enhanced by the oxidized species attached on Pt surface as electrophilic or Lewis sites [10] because the electropositive oxides may adsorb and activate C=O bond via the unoccupied electron pair of oxygen. For the bimetallic catalysts prepared by IMP, promoters lack of close contact with Pt, and adding the second metal does not have substantial influence on the EAS area, which can hardly contribute to the activation of C=O for hydrogenation (as illustrated in Scheme 4.1c). Furthermore, the metal oxide layer (or small clusters) deposited on

CNTs surfaces may hinder the adsorption of CALD via π - π interaction, resulting in the extremely low activities for impregnated bimetallic catalysts.

The CO stripping measurements show that the onset potentials for CO oxidation on PtFe/CNT-973 and PtCo/CNT-973 shift negatively (see Figure 4.8), implying the promoted CO oxidization. The hydroxyl groups generated by water dissociation can adsorb on the surface of metal oxide species [37], and these adsorbed hydroxyls (OH_{ads}) may be involved in CO stripping and facilitate the oxidation of CO on a Pt surface [38]. Therefore, the negative shift of CO oxidization potential further demonstrates the close contact between metal oxide and Pt nanoparticles. On the contrary, the onset and peak potentials of CO oxidation for the impregnated catalysts are remarkably higher than Pt/CNT-973, as shown in Figure 4.8, suggesting that impregnated Fe or Co mainly modifies the surface properties of CNTs rather than Pt nanoparticles. The promoting effect of metal oxide on CO oxidization is based on the assumption that Pt particles are adjacent to the metal oxide promoters [38]. If the metal oxide locates apart from Pt active sites, and disperses primarily on CNTs surfaces, OH_{ads} can hardly participate in the CO oxidization due to the segregated distribution of Pt and metal oxide clusters (see Scheme 4.1c, left). The CNTs conductivity may also be altered due to the coverage of metal oxide with OH_{ads} . Therefore, the CO oxidation is impeded by the decreased charge transfer capability of CNTs, resulting in the positive shift of oxidization potential for impregnated catalysts.

Figure 4.8 CO stripping voltammograms of PtFe/CNT-973, PtCo/CNT-973, Pt/CNT-973, PtFe/CNT-973-IMP and PtCo/CNT-973-IMP. The left and right dash lines indicate the onset and peak potentials of Pt/CNT-973, respectively.

CV profiles of these catalysts show that Pt-O reduction peak potentials for Fe- and Co-promoted catalysts prepared by MAPR shift negatively as compared to Pt/CNT-973, while Pt-O reduction peak potentials of corresponding impregnated bimetallic catalysts either remain constant or shift positively (see Figure 4.9). Metal oxide islands on Pt nanoparticles may change the interaction between catalytic active sites and support, e.g., the electron flux from CNTs to Pt nanoparticles under certain given

potential. The current flow in response to applied potential may be diminished by metal oxide species enriched on Pt particles, which decreases the number of available electrons for Pt-O reduction. For the impregnated bimetallic catalysts, the addition of promoters mainly contributes to the modification of support surface properties. Agglomeration of metal oxides with surface adsorbed OH_{ads} decreases the conductivity of CNTs support (evidenced by CO stripping), which may also impair the current flow towards Pt nanoparticles. Nevertheless, it also makes the catalyst surface more hydrophilic and more accessible to water which facilitates Pt-O reduction as interpreted in Equation (4.1) and (4.2), i.e., leading to a less negative reduction potential.

Figure 4.9 Shift of Pt-O reduction Peaks for PtFe/CNT-973, PtCo/CNT-973, PtFe/CNT-973-IMP and PtCo/CNT-973-IMP, comparing to Pt/CNT-973.

The existence of Co or Fe metallic phase alloyed with Pt after reduction cannot be completely ruled out in this one-step preparation and reduction. Therefore, two kinds of electron transfer mechanisms should be considered, one is from CNTs support to metal active sites [6], the other is from promoter to Pt in the alloy [3, 39]. Herein, XPS was employed to investigate the electron and oxidization states of Pt and promoters. To determine the peak position accurately, the XPS profiles were fitted by Gaussian-Lorentzian sum function. As shown in Figure 4.10a, Pt 4f_{7/2} binding energies of impregnated catalysts shift towards higher value as compared to those of Pt/CNT-973, suggesting that Fe or Co oxides dispersed on CNTs surfaces may hinder the electron transfer from CNTs to Pt, as donating electrons to Pt leads to the negative shift of Pt binding energy [9]. For bimetallic catalysts prepared by the MAPR method, Pt 4f_{7/2} binding energies are lower than that of Pt/CNT-973, which can be ascribed to the electron transfer from promoters to Pt due to the formation of alloy. The XPS spectra (Figure 4.10b) show that nearly all the iron exists as metal oxide [40], and a shoulder peak at 707.85 eV is discernable for the Fe 2p spectrum of PtFe/CNT-973. This binding energy is slightly larger than 2p_{3/2} binding energy of metallic iron (706.8 eV) [40], which can be attributed to the formation of Pt-Fe alloy [41]. This shoulder peak is not obvious for PtFe/CNT-973-IMP. In the XPS spectra of Co 2p (Figure 4.10c), the main peak centered at around 781 eV can be assigned to cobalt oxide species [42]. The broadening of cobalt peak for PtCo/CNT-973 may be due to the existence of metallic cobalt, which has the binding energy of *ca.* 778 eV [42].

Figure 4.10 XPS spectra of (a) Pt, (b) Fe and (c) Co on Pt/CNT-973, PtFe/CNT-973, PtCo/CNT-973, PtFe/CNTS-973-IMP and PtCo/CNT-973-IMP.

In addition to the XPS measurements, an equilibrium adsorption constant of toluene and benzene ($K_{T/B}$) is used to characterize the electron density of Pt nanoparticles in the presence of promoters. $K_{T/B}$, which is derived from the relative hydrogenation rates of toluene and benzene (see Chapter 3 Equation 3.3), is only correlated with reaction temperature and independent on other variables including particle size and support [43]. As the electron donation is easier for toluene compared to benzene, a larger $K_{T/B}$ value suggests a lower electron density of Pt nanoparticle [43]. As shown in Figure 4.11, the lower $K_{T/B}$ value (3.24) of PtFe/CNT-973 as compared to that of Pt/CNT-973 (4.28) implies that electrons are transferred from Fe to Pt in this bimetallic catalyst. The increased electron density of Pt nanoparticles attenuates the binding energy, particularly that of C=C bond, and favors the hydrogenation of C=O [10]. The promoted CALC selectivity contributed by the electron transfer from iron to platinum was also detected by the X-ray absorption measurements on a carbon supported Pt-Fe alloy [3]. The electron transfer from Co to

Pt is relatively poorer as evidenced by the larger $K_{T/B}$ value for PtCo/CNT-973 (3.57). Less resistance towards the hydrogenation of C=C bonds leads to the formation of more HALD and HALC, which compromises the selectivity of CALC (see Table 4.5). For the impregnated catalysts, electron transfer from Co to Pt is also detected because of the lower $K_{T/B}$ value of PtCo/CNT-973-IMP (3.67). The discrepancy regarding the Pt 4f binding energy may be due to the low metal loadings. However, the electron transfer in PtCo/CNT-973-IMP is less pronounced as compared to PtCo/CNT-973, due to the lack of close contact between Co and Pt. For PtFe/CNT-973-IMP, the $K_{T/B}$ value (4.49) is even larger than that of Pt/CNT-973, implying that there is no electron transfer from Fe to Pt. Additionally, Fe species enriched on the support surface may hamper the electron transfer from CNTs to Pt. The electron deficiency of Pt nanoparticles on PtFe/CNT-973-IMP promotes the formation of HALD and decreases the selectivity of CALC (see Table 4.5).

Figure 4.11 Relative benzene hydrogenation rate vs. ratio of its partial pressure at 308

K. $K_{T/B}$ values of tested catalysts are slopes of lines.

4.4 DoE for three-metal catalytic system

It is found from Table 4.5, the selectivity towards CALC can be promoted by adding Fe promoter, while introducing Co is beneficial to the catalytic activity. It is postulated that combining Fe and Co promoters to the Pt active sites may enhance both catalytic activity and CALC selectivity. However, it is extremely time-consuming to develop a three metals (Pt, Fe and Co) catalyst by using one-factor-at-a-time (OFAT) method which ignores the correlations among metals. Herein, the design of a three-metal catalyst with both high selectivity and activity is attempted using a rational screening methodology. HSS was employed to screen the loadings of promoters while maintaining the content of Pt (5 wt.%) constant. HSS provides a good coverage of the factor space with minimum number of design points [44]. HSS design is based on the

rewritten of integer, that any integer n can be rewritten in a radix notation of another integer R as follows:

$$\begin{aligned} n &\equiv n_0 n_1 n_2 \dots n_{m-1} n_m \\ &= n_m + n_{m-1}R + n_{m-2}R^2 + \dots + n_1 R^{m-1} + n_0 R^m \end{aligned} \quad (4.3)$$

where m is the integer part of $\log_R n$. The inverse radix function of n , can be constructed by reversing the order of the digits of n and concatenating them behind a decimal point:

$$\begin{aligned} \psi_R(n) &= 0.n_m n_{m-1} \dots n_2 n_1 n_0 \\ &= n_m R^{-1} + n_{m-1} R^{-2} + \dots + n_1 R^{-m} + n_0 R^{-m-1} \end{aligned} \quad (4.4)$$

Therefore, for a n design points situation whose dimension is d , need to be set by HSS design, then the first $d - 1$ prime numbers should be selected as the integer R in Equation 4.3: $R_1, R_2, \dots, R_{d-1}$. The design points can be allocated by

$$\mathbf{x}_i = \mathbf{1} - \left[\frac{i}{n}, \psi_{R_1}(n), \psi_{R_2}(n), \dots, \psi_{R_{d-1}}(n) \right]^T \quad (4.5)$$

where $i = 1, 2, \dots, n$ and $\mathbf{1}$ is a unity vector.

The distribution of experimental points in the two dimensional factor-space is shown in Figure 4.12. The best result (conversion = 71.3%, selectivity = 89.3%) is obtained when the weigh loadings of Fe and Co are 1.25 and 0.5 wt.%, respectively.

Figure 4.12 Design points allocated by HSS method for optimizing a three-metal catalyst.

4.5 Discussion

It has been demonstrated that electrochemistry measurements including CV and CO stripping serve as complementary approaches to investigate the surface properties of CNTs supported catalysts. Based on the characterization and chemically probed reaction results, it can be concluded that surface oxygen-containing groups can be efficiently removed from CNTs surfaces by the high-temperature treatment. Elimination of these groups suppresses acid-catalyzed side reactions, enhances the adsorption of CALD and electron transfer from CNTs to Pt, resulting in substantially increased activity and selectivity to CALC. By screening various kinds of solvents, a dramatic increase of TOF as well as selectivity is observed when using EA as the solvent. It is proposed that in addition to the direct hydrogenation by H atoms adsorbed on Pt nanoparticles, transfer hydrogenation between CALD and EA occurs, in which EA can be partially reduced to afford a hemiacetal intermediate. Subsequent

hydrogen transfer from this intermediate to CALD contributes to the high activity and selectivity.

The superior activity and selectivity for CALD hydrogenation over bimetallic catalysts synthesized by MAPR are ascribed to the close contact between promoters and Pt nanoparticles. The concept of “close contact” has been suggested by Plomp et al., in which the promoter (tin or gallium) was reduced by the hydrogen dissociated on pre-formed Pt particles [4]. Similarly, Co-decorated Pt nanoparticles were also synthesized by reducing Co in a suspension of Pt particles prepared in advance; an organic additive, 1,2-hexadecanediol was employed as the reducing reagent [1]. Both examples require two successive reduction steps, one for the formation of Pt nanoparticles and the other for the reduction of promoters in the presence of Pt nanoparticles. In this microwave-assisted synthesis, the bimetallic catalysts with close contact between active sites and promoters can be prepared in one step. The reduction potential of platinum (1.188 V) is higher than that of iron (-0.440 V) and cobalt (-0.277 V) [45]; there is a high probability that Pt can be readily reduced by EG prior to the reduction of Fe or Co (see Scheme 4.2a). It has been demonstrated that Co cannot be reduced in the absence of Pt particles when diol was the reducing agent [1]. Under a high temperature (433 K), EG may interact with Pt ions, resulting in the oxidation of EG to aldehyde, glycolic, oxalic acid, or even CO₂. The electrons donated from these oxidation reactions lead to the reduction of Pt cations [7]. Once the Pt particles form, the oxidation of EG may take place via an alternative or parallel reaction pathway that involves the hydrogen abstraction from EG by platinum [7]. Thus, the hydrogen atoms adsorbed on Pt nanoparticles may facilitate the reduction and deposition of the second

metal (Fe or Co) on Pt surfaces (see Scheme 4.2b), which is similar to the reduction steps in the RDP method reported by Plomp et al. [4]. Further reductions of Pt and transition metal precursors afford the formation of alloys (see Scheme 4.2c). Once the catalysts are exposed to air, Fe or Co metal on the Pt surface will be rapidly oxidized (see Scheme 4.2d).

Scheme 4.2 Synthesis of bimetallic catalyst by using MAPR method.

By employing the MAPR method, promoters are prone to closely interact with Pt active sites, which are essentially evidenced by CO stripping and CV measurements. The enrichment of promoters on Pt catalytic sites attains the hydrophobic surface of

CNTs which is beneficial to the adsorption of CALD reactants. In addition, the synergistic effects including activation of C=O bond and efficient metal-to-metal electron transfer (evidenced by $K_{T/B}$) remarkably enhance the catalytic activity and selectivity due to the close contact between Pt and promoter. For impregnated catalysts, promoters primarily disperse on the surface of CNTs, which blocks the adsorption of CALD, resulting in low activities. Segregation of promoter and Pt active site diminishes the electron transfer from promoter to Pt, even hinders the electron donation from CNTs to Pt. Pt nanoparticles with low electron density cannot efficiently inhibit the reduction of C=C bonds, resulting in a low selectivity towards CALC.

4.6 Summary

In this chapter, Pt-based mono and bimetallic catalysts were synthesized by employing a facile and rapid MAPR method. These catalysts were successfully applied to the selective hydrogenation of CALD to CALC. The hydrogenation results highly depended on the surface properties of the CNTs support, solvent and promoter. Removal of oxygen-containing groups from CNTs surfaces elevated both activity and selectivity, due to the suppressed side reactions catalyzed by acid and enhanced electron transfer from CNTs to Pt nanoparticles. By screening solvents with different polarities, EA was identified as the best candidate in this reaction and the enhanced activity is hypothesized to result from the presence of parallel transfer hydrogenation steps. The catalytic properties can be promoted by Fe and Co. Compared to IMP preparation, MAPR not only served as a facile and timesaving synthesis methodology, but also afforded close contact between promoters and Pt nanoparticles, which attains

the affinity between CNTs and CALD due to the π - π interaction and assists the metal-metal electron transfer. These synergic effects contributed to the significantly improved activity and high selectivity. This work has been published in Journal of Catalysis (Guo et al. Journal of Catalysis, 2010, 276, 314–326); reuse in this chapter is under the permission of Elsevier Global Rights Department.

List of abbreviations

CALC	Cinnamal Alcohol
CALD	Cinnamaldehyde
CNF	Carbon Nano-Fiber
CNTs	Multi-Walled Carbon Nanotubes
CV	Cyclic Voltammogram
EA	Ethyl Acetate
EAS	Electrochemical Active Surface
EG	Ethylene Glycol
GC-MS	Chromatography-Mass Spectrometry
HALC	Hydrocinnamal Alcohol
HALD	Hydrocinnamaldehyde
HDP	Homogeneous Deposition Precipitation
HSS	Hammersley Sequence Sampling
IMP	Impregnation
MAPR	Microwave-Assisted Polyol Reduction
RAIRS	Reflection-Absorption Infrared Spectroscopy
RDP	Reductive Deposition Precipitation
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TOF	Turnover Frequency
XPS	X-ray Photoelectron Spectroscopy
XRD	X-Rays Diffraction

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Chapter 5 Synthesis of Chiral Mesoporous Silica Materials and Their Applications in Asymmetric Hydrogenation of Dimethyl Itaconate and Enantioselectively Controlled Release of Racemic Metoprolol

Methodologies for obtaining enantiomerically pure drugs are highly desirable in the pharmaceutical industry because synthesized drugs are invariably racemic mixtures and usually only one of the enantiomers is clinically efficacious [1]. Enantioselective adsorption of racemic drugs was accomplished on amorphous chiral silica materials synthesized using chiral surfactants as directing reagents [2-4]. These materials have demonstrated ability to enantio-selectively adsorb chiral drugs which have no specific similarity with the chiral directing reagents. Asymmetric synthesis is considered as a feasible way to produce enatio-pure substances in a large scale, which depends on the development of chiral catalysts comprising carefully designed chiral ligands [5]. In contrast, report on the utilization of chiral support in asymmetric catalysis is limited. Enlightened by the asymmetric hydrogenation catalyzed by palladium adsorbed on a nature chiral support—silk [6], we postulate the possibility to design and synthesize achiral Pt nanoparticles supported on a synthesized chiral support for asymmetric hydrogenation.

Recently well-ordered chiral mesoporous silica (CMS) materials with either left- or right-handed helix channels have been successfully synthesized by adopting chiral surfactants as templates [7-11]. These inorganic chiral materials attract more and more attentions, due to their potential applications in both chiral separation and asymmetric catalysis. Wu et al. reported the first preparation of chiral mesoporous silica nanotubes using achiral surfactants in the presence of a chiral amino alcohol, which afforded a

new approach for the synthesis of chiral mesoporous materials with helical channels in enantiomeric excess [10]. However, applications based on these CMS materials have not been reported extensively

In this chapter, we develop a novel method to synthesize a series of CMS materials, including chiral MCM-41 (denoted herein as CMCM-41), chiral SBA-15 (CSBA-15), and chiral SBA-16 (CSBA-16), employing conventional achiral surfactants as the templates and a chiral cobalt complex $\Lambda\text{-[Co((+)chxn)}_3\text{]I}_3$ (chxn = *trans*-1,2-diaminocyclohexane, denote this metal complex as CCC here) as the co-template, shown in Scheme 5.1. Platinum metallic nanoparticles are loaded on CMCM-41 by employing microwave-assisted polyol reduction (MAPR) method, and asymmetric hydrogenation of dimethyl itaconate over CMCM-41 supported Pt is tentatively investigated. Although the enantio-bias aroused from the chiral silica support is extremely low, absence of any enantio-selectivity for achiral mesoporous silica supported Pt nanoparticles may underpin the role played by chiral support during asymmetric hydrogenation. To further substantiate the chirality of CMS materials, these mesoporous silica are used as carriers for the controlled release of a representative chiral drug metoprolol (used in the treatment of the cardiovascular system, see Scheme 5.1). In comparison with the corresponding achiral mesoporous silica (ACMS), all CMS materials exhibited remarkably different drug release kinetics for enantiomers of metoprolol, which may be ascribable to the chiral selective interaction between CMS materials and enantiomers. The local chirality in the synthesized CMS materials was also corroborated by vibrational circular dichroism

(VCD) characterization. We speculate herein that the chirality of chiral co-template can be transferred to the building blocks of mesoporous silica.

Scheme 5.1 Molecular structures of CCC and metoprolol (top); Scheme of synthesis of CMS (middle); Scheme of asymmetric hydrogenation of dimethyl itaconate (bottom).

5.1 Physical properties of CMS and ACMS materials

Figure 5.1 CD spectrum and geometrical structure of Λ -[Co(+)(chxn)₃]I₃ (CCC).

The geometrical structure and CD spectrum of purified CCC are shown in Figure 5.1. Three absorption bands at 350, 443, and 500 nm are contributed by the electronic transitions of $^1A_{1g} \rightarrow ^1T_{2g}$, $^1A \rightarrow ^1A$, and $^1A \rightarrow ^1E$, respectively [12]. Calculated purity of as-synthesized Λ -[Co(+)(chxn)₃]I₃ is 97%.

Figure 5.2 FTIR spectra of CMS materials before and after removal of organic templates: a is CCC; b, c and d are as-synthesized CMCM-41, CSBA-15 and CSBA-16, respectively; e, f and g are template-free CMCM-41, CSBA-15 and CSBA-16, respectively.

The removal of template and CCC was confirmed using FTIR (see Figure 5.2). In the infrared spectra of as-synthesized CMS materials, the absorption bands presenting at 2930 cm^{-1} and 2860 cm^{-1} can be attributed to the asymmetric and symmetric stretching of CH_2 , respectively; the band at 1470 cm^{-1} has been assigned to the deformation of CH_2 [13]. Absence of these absorption bands in the infrared spectra of template-free CMS materials suggests the complete removal of organic templates and CCC after 8 runs of solvent extraction. The absence of cobalt metal was also confirmed by ICP measurement.

Figure 5.3 XRD patterns of CMS and ACMS materials.

The template-free CMS materials were characterized using low-angle XRD and nitrogen physisorption, as shown in Figure 5.3 and Figure 5.4, respectively. Both low-angle XRD and nitrogen physisorption results suggest that highly ordered mesoporous structures have been successfully synthesized. Four well-resolved diffraction peaks in the XRD patterns of CMCM-41 (Figure 5.3a) and CSBA-15 (Figure 5.3b) evidence the formation of highly ordered mesostructure with hexagonal symmetry ($p6mm$). In the XRD pattern of CSBA-16, four diffraction peaks can be discerned in the 2θ range of $1-2^\circ$, indexed as (110), (200), (211) and (220) reflections corresponding to the center cubic ($Im3m$) pore arrangement with a lattice constant of $a_0 = 12.2$ nm (Figure 5.3c). As shown in Figure 5.3, the corresponding ACMS materials, including MCM-41, SBA-15 and SBA-16, are also successfully synthesized in the absence of CCC. Nitrogen adsorption-desorption isotherms of CMS and ACMS materials show sharp step increases, which can be attributed to the capillary condensation of nitrogen in the regular mesopores (see Figure 5.4). Both CMS and ACMS materials synthesized in this study possess narrow pore size distributions as shown Figure 5.4b, d and f.

Figure 5.4 Nitrogen physisorption isotherms (left) and pore size distributions (right) of CMS and ACMS materials.

The textural properties of various samples (CMS and ACMS) are summarized in Table 5.1. The samples show large specific surface area, pore volume and different pore diameters. CMS materials exhibit similar structural parameters compared to their achiral counterparts. MCM-41 and CMCM-41 possess the largest surface area ($> 1000 \text{ m}^2/\text{g}$) but the smallest pore diameter ($\sim 2 \text{ nm}$), whereas CSBA-15 and SBA-15 show the largest pore size ($\sim 6 \text{ nm}$) and pore volume ($> 1.4 \text{ cm}^3/\text{g}$). Pore sizes of CMS materials are slightly larger than those of corresponding ACMS materials, which may be due to the insertion of CCC into micelles, resulting in the template larger in diameter.

Table 5.1 Textural parameters of CMS and ACMS materials.

CMS	Surface area	Pore volume	Pore size	a_0^a
	(m^2/g)	(cm^3/g)	(nm)	(nm)
CMCM-41	1174	0.92	2.2	4.8
CSBA-15	974	1.44	6.0	10.8
CSBA-16	950	0.83	3.7	12.2
MCM-41	1216	1.46	2.1	4.5
SBA-15	809	1.34	5.8	10.2
SBA-16	712	0.64	3.6	11.9

^a For CMCM-41 and CSBA-15, $a_0 = 2/\sqrt{3} \times d_{100}$; for CSBA-16, $a_0 = \sqrt{2} \times d_{110}$.

Particle sizes and size distributions of CMS materials were determined by dynamic light scattering (see Figure 5.5a, d and g). The particle diameters of CMS materials range between $0.7 - 1.5 \text{ }\mu\text{m}$. These results are further validated by SEM characterization as shown in Figure 5.5b, e and h. The bean-like particles of CMCM-

41 and CSBA-15 are monodispersed; whereas the bean-like particles of CSBA-16 agglomerate to some extent. It is worth noting that no helical morphology can be observed in these CMS materials, which is distinct from the CMS reported in previous literatures [7-11]. The nanoscale pore structures of CMS materials are reinforced using TEM. Typical TEM micrographs (Figure 5.5c, f and i) depict the well-ordered pore structures which complement the analysis on the pore sizes estimated by nitrogen physisorption and XRD analysis.

Figure 5.5 Particle size distributions (left), SEM (center) and TEM (right) micro-images of CMCM-41 (a, b, c), CSBA-15 (d, e, f) and CSBA-16 (g, h, i).

5.2 Asymmetric hydrogenation of dimethyl itaconate over Pt/CMCM-41

Since enantio-bias in asymmetric hydrogenation could be solely attributed to a nature chiral support when silk supported Pd particles were employed as catalysts [6], it should be interesting to apply CMS material on asymmetric catalysis system. Pt nanoparticles were loaded onto CMCM-41 by employing the MAPR method, and the as-synthesized chiral silica supported catalyst was attempted in the asymmetric hydrogenation of dimethyl itaconate. The effects of temperature, hydrogen pressure and Pt loading were studied as shown in Table 5.2. The catalyst shows enantioselectivity although it is rather poor. Low Pt loading slightly improves the enantioselectivity. This may imply that the chiral discrimination can only occur at several nano-meter scale or molecular level. The highest enantio-excess ($ee = (R-S) \times 100\% / (R+S)$) of 1.4% for this chemically probed reaction was obtained at a low temperature, hydrogen pressure and Pt loading, while conversion decreases accordingly. No enantio-bias can be found under the optimized conditions by using achiral MCM-41 as support. These observations may evidence the existence of chiral environment in our CMS material and suggest that the CMS support does play a role in the asymmetric hydrogenation process. As even the most effective catalyst is usually effective for one or one kind of asymmetric reactions, screening of various asymmetric catalysis systems are undergoing.

Table 5.2 Results of asymmetric hydrogenation of dimethyl itaconate by using CMCM-41 supported Pt particles.

Entry	Pt loading (wt.%)	Temperature (°C)	H ₂ Pressure (bar)	Conversion ^a (%)	ee ^b (%)
1	2	25	5	100	0
2	2	0	5	23.6	0.3
3	0.5	25	5	4.4	0.6
4	0.5	0	5	1.7	1.0
5	0.5	0	2	1.6	1.4
6 ^c	0.5	0	2	1.8	0

^a Determined by gas chromatograph ;

^b $ee = (R-S) \times 100\% / (R+S)$ (see Chapter 3 Equation 3.4);

^c the results of Pt based catalyst using achiral silica as support.

5.3 Characterization of the chirality of CMS materials by controlled release of racemic metoprolol

The controlled release system may have significant practical meanings if chiral therapeutic drugs were chosen as model molecules. Because many drugs may not perform their pharmacological activities in a very effective way, due to the *in vivo* rapid excretion and decomposition rates and lack of specific affinity to the site of action [14]. Since the first report using MCM-41 as a novel drug carrier by Vallet-Regí et al. [15], several mesoporous silica materials have been investigated [16-19]. Mesoporous silica nanoparticles with various morphologies (including sphere, ellipsoid, rod and tube) and pore configurations (including cylindrical, helix and wormlike) were synthesized and employed as nano-carriers for controlled release

[16]. Nevertheless, the application of CMS in this research area is rarely investigated. Aiming to further substantiate the existence of chirality in these prepared mesoporous silica, kinetic release of a representative chiral drug metoprolol was investigated using CMS materials and their achiral counterparts as carriers.

For typical controlled releasing process, 52 mg of racemic metoprolol was dissolved in 6 g of EtOH. 50 mg of CMS or ACMS (after template removal) was mixed with the racemic metoprolol solution under vigorous stirring at room temperature for 24 h. The solids were collected by centrifuge and dried under vacuum at ambient temperature. Concentrations of R- and S- enantiomers in filtrate were measured using high performance liquid chromatography (HPLC, Angilent 1100 series) with a Chiralpak AD[®] column (250 × 4.6mm, Daicel Chemical Industries). Release profiles were obtained by immersing the above CMS or ACMS materials loaded with metoprolol in 5 g of EtOH. The amount of released metoprolol (including two enantiomers) was measured using the same HPLC.

The total release profiles of metoprolol including both R- and S- enantiomers are shown in Figure 5.6. The drug release progression is composed by an initial burst release and a subsequent retarded release for all the carriers in this study. The release of drugs at initial stage can be attributed to the rapid delivery of drug molecules adsorbed on the outer surface of carriers [20]. The release of metoprolol from CSBA-15 and SBA-15 is remarkably faster than that from other mesoporous silicas with smaller pore diameters, regardless of the carrier is chiral or achiral. It is generally accepted that small pore size may restrict the release of drug molecules, and similar

observations have been reported elsewhere [17, 18]. Interestingly, CMS material shows a more rapid release of drugs compared to the corresponding ACMS although the pore sizes are similar (see Table 5.1). This may be due to the poor compatibility or miscibility between one of metoprolol enantiomers and CMS matrix. If CMS materials are prone to adsorb one of the two metoprolol enantiomers, the metoprolol molecules may not disperse homogeneously on the surface, resulting in the initial burst release due to the microscopic phase-separation [21]. It is noteworthy to mention that the difference in release behavior over CMCM-41 and CSBA-16 are smaller compared to that of MCM-41 and SBA-16, implying that besides the pore size effect, the release rate may also be controlled by other factors (i.e. the chiral interaction) in CMS channels.

Figure 5.6 Kinetic release profiles of metoprolol (including both R- and S-enantiomers) from CMS (a) and ACMS (b) materials.

The release profiles of different enantiomers were also studied, as shown in Figure 5.7. It is observed that the R- and S- enantiomers adsorbed on CMS materials exhibit noticeably different release behaviors (see Figure 5.7a, b and c). In contrast, when the ACMS counterparts were employed as drug carriers, the release profiles of two enantiomers are almost identical (see Figure 5.7d, e and f). Furthermore, all CMS carriers show stronger adhesive capability to S- enantiomer than that to R- enantiomer, although these CMS materials possess different surface areas, pore sizes and pore structures. The difference of kinetic release between two enantiomers loaded on CMS materials may be attributed to the specific local chirality on the pore wall surface of these carriers. For CMCM-41 and CSBA-16, the chiral discrimination can hardly be observed within first 4 h and become distinct in the sustained release stage, suggesting that the chiral interaction mainly exists in the mesopores of CMS materials because the later release stage is attributed to the delivery of drugs adsorbed inside the mesoporous channels [22]. Notably, the chiral discrimination of CMS materials increases with the pore diameter; and the best result is achieved on CSBA-15 with the largest pore diameter (as shown in Figure 5.7b). For CSBA-15, the chiral discrimination can even be observed at the initial stage of release profile (0.5 h). This may be due to the fact that large pore volume and pore size of CSBA-15 enable the accommodation of excessive amount of drugs inside the mesopore channels. Therefore, more chiral drugs can specifically interact with inner chiral surfaces of CSBA-15.

The release profiles of metoprolol from ordered mesoporous matrix can be modeled using the power law equation which has been widely used in controlled drug delivery system (DDS) using various kinds of materials as carriers, including polymers [21] and mesoporous silica [23]. The equation can be expressed as follows:

$$w_t/w_\infty = Kt^n \quad (5.1)$$

where w_t is the amount of drug released at time t and w_∞ is the total amount of drug initially adsorbed inside the matrix. K is a constant representing structural and geometric characteristic of drug carrier. n is the exponent of release kinetics which gives an indication of the drug diffusion. If n value is close to 0.5, the drug release simply follows a diffusion-controlled mechanism, namely the Fickian diffusion mechanism. Otherwise, the deviation extent of n value from 0.5 may suggest the degree of release behavior influenced by certain factors other than diffusion.

Figure 5.7 Kinetic release profiles of R- and S- metoprolol from CMS (a: CMCM-41, b: CSBA-15, c: CSBA-16) and ACMS (d: MCM-41, e: SBA-15, f: SBA-16) materials.

It has been reported that the desorption of drug from mesopore wall surface does depend on several factors besides the concentration gradient, such as molecular size of drug molecules, surface chemistry of pore wall, interaction between drug and pore wall surface, even the tortuosity of the mesoporous channels [20].

Table 5.2 Kinetic parameters of total metoprolol released from CMS and ACMS materials.

	CMCM-41	CSBA-15	CSBA-16	MCM-41	SBA-15	SBA-16
w_{∞} (mg)	20.91	20.83	20.19	20.29	27.49	19.58
K	68.53	89.86	72.46	53.33	62.56	36.94
n	0.086	0.023	0.071	0.089	0.118	0.136
r^2	0.978	0.984	0.995	0.989	0.980	0.955

Table 5.2 shows the values of n and K with corresponding correlation coefficient r^2 for total release of drugs from CMS and ACMS materials. Due to the complexity of DDS using mesoporous material as carrier, it is not surprised to find the n value in this study is significantly smaller than 0.5. Similar observations have also been reported by other groups when mesoporous silicas were employed as carriers, regardless of the carriers and the drugs [18, 23-25]. The values of n are generally smaller when using CMS material as carrier compared to the corresponding ACMS material. The larger deviation from Fickian diffusion for CMS materials than that of ACMS materials may imply the specific interaction between chiral drug molecules and CMS carriers with local chirality, the larger the deviation, the better the asymmetric discrimination. The values of release constant K for CMS materials are significantly larger compared to

ACMS materials, although their mesostructures are similar (see Table 5.1). The large K values of CMS may be attributed to the poor miscibility between metoprolol enantiomers and CMS matrix. As previously discussed, the inhomogeneous distribution of drugs may lead to initial rapid release. Therefore, although the mesostructure and composition of CMS and corresponding ACMS materials are comparable, the variation of surface property may give rise to the different release rates and K values.

We also compared the release profiles of R- and S-enantiomers of metoprolol. Both n and K values of R-enantiomer are generally larger than those of S-enantiomers, when CMS materials are employed as drug carriers (as shown in Table 5.3). These observations can be ascribed to the different affinity of R- and S-enantiomers to the CMS pore wall surfaces with certain local chirality, although the detail configurations of this local chirality remain unclear. A supportive evidence for such an argument is that a larger n value always presents along with a smaller K values for ACMS materials (MCM-41 and SBA-15), or they are almost identical (SBA-16), suggesting no selective interactions between ACMS materials and R- and S-enantiomers of metoprolol.

Table 5.3 Kinetic parameters of R- and S-enantiomers of metoprolol released from CMS and ACMS materials.

	CMCM-41		CSBA-15		CSBA-16		MCM-41		SBA-15		SBA-16	
	R	S	R	S	R	S	R	S	R	S	R	S
$w_{\infty}(\text{mg})$	10.63	10.34	10.52	10.31	10.38	9.91	10.20	10.09	13.81	13.68	9.91	9.68
K	68.28	67.97	92.19	87.67	72.52	72.48	56.75	57.46	69.13	70.07	42.10	41.99
n	0.076	0.072	0.022	0.019	0.073	0.068	0.100	0.098	0.098	0.096	0.103	0.103
r^2	0.995	0.994	0.966	0.981	0.992	0.991	0.981	0.981	0.991	0.990	0.924	0.926

Due to the fast release rate at initial stage and some experimental limits, it is difficult to measure the amount of drug when w_t/w_∞ is less than 0.6 (see Figure 5.6 and 5.7). Some reports suggested that the power law equation can only be applied when w_t/w_∞ is beyond 0.6 [21, 24]. In this study, the release profiles of metoprolol from the ordered mesoporous matrix were also fitted using Noyes–Whitney equation averaged over a small volume in the following manner [20, 26]:

$$w_t/w_\infty = A[1-\exp(-k_1t)] \quad (5.2)$$

where $A = (w_t/w_\infty)_{\max}$ is the maximum percentage of drug released, w_t is the drug released at time t and w_∞ is the total mass of drug initially adsorbed inside the matrix. k_1 is the diffusion coefficient in mesoporous channels which is assumed to be independent of the drug concentration. This model has been applied to the drug release from mesoporous silica reported by some previous studies [20, 27, 28].

However, it was found that the release profiles in our study do not follow the ideal diffusion controlled simulation represented by Equation (5.2). The desorption of drug from mesopore wall surface depends on several other factors such as molecular size of drug molecules, surface chemistry of pore wall, interaction between drug and pore wall surface, even the tortuosity of the mesoporous channels [20]. Hence, a modified equation was applied to simulate the release of metoprolol by introducing an empirical non-ideality factor δ to Equation (5.2), which has been reported by Vallet-Regí et al. [20]. Equation (5.2) is transformed into the following expression:

$$w_t/w_\infty = A[1-\exp(-k_1t)]^\delta \quad (5.3)$$

Table 5.4 Kinetic parameters of total metoprolol released from CMS and ACMS materials.

	CMCM-41	CSBA-15	CSBA-16	MCM-41	SBA-15	SBA-16
w_{∞} (mg)	20.91	20.83	20.19	20.29	27.49	19.58
A (%)	91	96	100	67	92	55
$k_1 \cdot 10^3$ (h ⁻¹)	80	93	69	298	59	168
δ (nm)	0.11	0.03	0.07	0.26	0.14	0.26

The value of δ varying between 1 and 0 indicates the deviation of proposed model from theoretical first order release kinetics. As shown in Table 5.4, values of δ calculated from total release profiles of metoprolol (regardless the R- and S-enantiomers) are generally smaller when CMS materials were used as carriers compared to those obtained when ACMS materials were used. The larger deviation for CMS materials than that of ACMS materials may suggest the specific interaction between chiral drug molecules and carriers with local chirality. The larger A values and smaller k_1 values (except CSBA-15) of CMS materials comparing to those of ACMS materials also indicate different surface properties, although the composition of these two materials are the same.

Table 5.5 Kinetic parameters of R- and S- metoprolol released from CMS and ACMS materials.

	CMCM-41		CSBA-15		CSBA-16		MCM-41		SBA-15		SBA-16	
	R	S	R	S	R	S	R	S	R	S	R	S
w_{∞} (mg)	10.6	10.3	10.5	10.3	10.3	9.9	10.2	10.0	13.8	13.6	9.9	9.6
A (%)	91	90	99	95	95	93	72	72	95	95	56	56
$k_1 \cdot 10^3$ (h ⁻¹)	86	77	58	30	52	22	78	74	84	89	182	182
δ (nm)	0.11	0.10	0.03	0.02	0.08	0.07	0.09	0.09	0.14	0.14	0.18	0.18

We also compared the release profiles of R- and S- metoprolol enantiomers. Δ and δ values of R- metoprolol enantiomer are generally larger than those of S- enantiomers, when CMS materials are used as drug carriers (as shown in Table 5.5). The diffusion coefficients (k_1) are also substantially different for R- and S- enantiomers. These observations can be ascribed to the different affinity of R- and S- enantiomers to the CMS pore wall surfaces with certain local chirality, although the detail configurations of this local chirality remain unclear. A supportive evidence for such an argument is that these coefficients for ACMS materials are almost identical suggesting no selective interactions between ACMS materials and R- and S- enantiomers of metoprolol.

These findings demonstrated the existence of a local chiral environment and the enantioselectivity of CMS materials for an enantiomeric pair. It should be noted that CMS materials synthesized in this study are capable of recognizing chirality of the drug molecule (metoprolol) that has no structural similarity to the CCC co-template (see Scheme 5.1). This is different from the enantioselectivity towards enantiomers of imprinted molecules reported previously [29-31]. In this study, the enantioselective discrimination mechanism may be similar with that of asymmetric adsorption of chiral molecules using chiral amorphous silica [2-4] or *d*- and *l*- quartz powders as adsorbents [32]. The asymmetric selectivity of these adsorbent materials derives from the chiral building blocks of silica, such as chirally metamorphosed SiO₄ tetrahedron or the four-SiO₄ segment helix which was found as the most abundant chiral units within quartz [33]. We speculate herein that the specific effect of local chiral environment on the two enantiomers of metoprolol is originated from the chiral silica backbone. The chiral entities on the surface of CMS materials can be distorted SiO₄

tetrahedron or chiral oligomers of SiO_4 induced by the chiral co-template. There are specific inter-ionic and hydrogen bonding interactions between chiral silica entities and functional groups of metoprolol (such as amine and hydroxyl groups), resulting in different adsorption capability between S- and R-enantiomers. As the structure of CCC molecule contains both hydrophobic and hydrophilic parts (see Scheme 5.1), CCC molecule may act like a surfactant and assemble with other achiral surfactants to embrace the channels of CMS materials; and meanwhile induce the formation of chiral silica entities. Therefore, the most probable location of chiral entities should be inside the channels of CMS leading to more S-enantiomers adsorbed inside the pores. This explains why the miscibility of metoprolol with CMS materials is poor and why both K and n values of R-enantiomers are larger than those of S-enantiomers in drug release profiles based on CMS materials. The different locations of enantiomers may also contribute to the preferentially delayed release for S- enantiomer compared to R-enantiomer.

5.4 VCD characterizations

To validate the existence of local chirality resulting from silica backbone, the characteristic of local chirality of CMS materials is further investigated using VCD spectroscopy. VCD is a circular dichroism spectroscopy in the infrared region; and it can be applied to retrieve conformational information of chiral materials [34-36]. Figure 5.8 shows the VCD and IR spectra of the template-free CMS materials. The strong band at *ca* 1080 cm^{-1} of VCD spectrum agrees well with IR absorbance, which is assigned to the Si-O asymmetric vibration [37]. In contrast, no VCD response is discernable in the mid-IR region for ACMS materials synthesized in the absence of

CCC co-template (see Figure 5.8). A plausible mechanism for the formation of local chirality on the CMS pore wall surface is that the building blocks of mesoporous silica, namely the SiO_4 tetrahedrons and silica oligomers ($\text{Si}(\text{OSi})_4$) are chirally distorted during the synthesis of CMS materials. These building blocks form chiral motifs on the pore wall surface [3], which contributes to the local chiral environment and the control over the enantioselective release of metoprolol.

Figure 5.8 VCD and IR spectra of the template-free ACMS and CMS materials.

5.5 Summary

In summary, a series of CMS materials with different pore sizes and structures were synthesized by adopting conventional achiral surfactant with CCC as co-template. The CMS channels exhibited local chiral characteristics which can be explained by the existence of the chirally distorted SiO_4 tetrahedrons and $\text{Si}(\text{OSi})_4$ formed during the

synthesis. Pt nanoparticles were loaded on the CMS material and applied in asymmetric hydrogenation. Although the enantio-excess was extremely low, the chiral induction capability of the catalyst should be contributed by the chiral support. The chirality of template-free chiral silica was further substantiated by enantio-selectively controlled release of chiral drug metoprolol. The different kinetic release profiles of R- and S-metoprolol from CMS materials can be attributed to the chiral interactions between enantiomers and local chiral bonding sites of chiral mesoporous matrix. This work has been published in Nanotechnology (Guo et al. Nanotechnology, 2010, 21(16), 165103/1-165103/11), reuse in this chapter is under the permission of IOP science publishing group.

List of abbreviations

ACMS	Achiral Mesoporous Silica
CCC	Chiral Cobalt Complex
CMS	Chiral Mesoporous Silica
DDS	Drug Delivery System
EtOH	Ethanol
<i>ee</i>	Enantio-Excess
HPLC	High Performance Liquid Chromatography
ICP	Inductively Coupled Plasma
MAPR	Microwave-Assisted Polyol Reduction
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscopy
VCD	Vibrational Circular Dichroism
XRD	X-Rays Diffraction

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Chapter 6 Understanding the Mechanism of Chirality Transfer in the Formation of Chiral Mesoporous Silica (MCM-41)

As discussed in Chapter 5, a family of chiral mesoporous silicas (CMS) including chiral MCM-41, SBA-15 and SBA-16 were synthesized by using achiral surfactants as template and a chiral cobalt complex (CCC) as the co-template. The existence of a chiral environment within the pores of these materials were evidenced by selective controlled release of enantiomers of chiral drugs. The conceptual study of chiral support in asymmetric hydrogenation was also attempted by loading Pt nanoparticles onto the CMS material. We proposed that the chirality of these CMS materials was derived from the silicate building blocks, i.e., asymmetrically distorted SiO_4 tetrahedrons or $\text{Si}(\text{OSi})_4$ oligomers formed during the synthesis. The chiral discrimination mechanism is similar to that of the chiral silica materials synthesized adopting molecular imprinting technique [1], but the difference is that our materials possess a general chirality, as they can enantioselectively adsorb chiral drug which has no specific structural similarity with the chiral co-template. At this stage, the detailed formation mechanism of chiral active sites in CMS materials still remains unclear.

Wu and coworkers reported the preparation of chiral mesoporous silica nanotubes using achiral surfactants in the presence of a chiral amino alcohol [2]. In their study, the chiral amino alcohol with stereogenic carbon interacted with achiral surfactants, induced the amphiphile conformation change in micelles, and facilitated the asymmetric alignment of micelles, which is similar to the phase transformation from an achiral nematic to a chiral cholesteric liquid crystal

induced by adding small chiral molecules [3]. The formation of helical channels largely relied on the macroscopic chirality of micelles imparted by the chiral dopant with a stereogenic center. It has been demonstrated that the amorphous chiral silica prepared by using chiral surfactants as directing reagents showed general enantioselectivity by discriminating enantiomers with diverse molecular structures, and the chiral entities of these amorphous silica were also assigned to chirally distorted SiO_4 tetrahedrons or $\text{Si}(\text{OSi})_4$ [4]. It was suggested that the protocol of chirality transferring from chiral surfactants to silica was reliant on either electrostatic or π - π interaction.

In our synthesis approach, compared to chiral amino alcohol and chiral surfactant, the most noteworthy feature of CCC is its propeller-like molecular configuration, namely its planar chirality. It has been demonstrated that the chiral metal complex can induce an asymmetric micro-environment in the inorganic framework [5]. Therefore, the unique chiral configuration of CCC may lead to a distinct self-assemble scheme between CCC and micelles. Additionally, we have to consider the interactions amongst three aspects including achiral surfactants, chiral co-templates and the building blocks of silica. As such, a precise elucidation of the chirality transfer steps would not be straightforward.

In this chapter, aiming to understand the mechanism of chirality transfer, several important preparation parameters which may significantly influence the property of chiral MCM-41 (CMCM-41) were investigated to afford an optimized synthesis approach. The chirality of template-free CMCM-41 was evidenced by enantioselective adsorption of racemic valine, which further substantiate the

general chirality of our CMS materials. Based on more detail investigations on chiral entities of CMS materials with the aid of vibrational circular dichroism (VCD) spectroscopy, we speculated that the chiral metal complex with rigid stereospecific structure may incorporate with micelles and thereafter distort the surfactants nearby, resulting in the formation of chiral aggregations composed of Λ -[Co(+)(chxn)₃]³⁺ and adjacent surfactant molecules. Subsequently, the chiral aggregations directed the formation of chiral entities (distorted SiO₄ tetrahedrons or Si(OSi)₄ oligomers) on the pore wall surface of mesoporous materials via electrostatic interaction. The macroscopic alignment of micelles was not affected at a low CCC concentration. The formation of chiral aggregations at a microscopic level was distinct from the chiral liquid crystal phase transformation of surfactants at a macroscopic level induced by adding soft and small chiral dopants with only a stereogenic carbon and a weak stereospecific effect.

6.1 Characterizations of CMCM-41

By optimizing the synthesis factors including temperature, ratio of CCC/silica and amount of ethyl acetate (EA) added, the VCD signal, i.e., the chirality of CMCM-41, can be improved as shown in Figure 6.1. In addition, the crystal morphology of CMCM-41 was also improved. SEM images (Figure 6.2a) reveal that the morphologies of deformed nano-rods either well dispersed or in the form of aggregation. As seen in Figure 6.2b, the resulted particles have twisted hexagonal rod-like morphology (with a hexagonal cross-section), 0.8-1.2 μm in outer diameter, and 2.0-2.5 μm in length. From six distinct surfaces, the helical pitch along the rod axis is estimated to be $\sim 15 \mu\text{m}$. In comparison to the chiral

mesoporous silica reported by Che and co-workers [6], the CMCM-41 prepared in this study is found to have relatively shorter average rod length and longer twist period. The overall handedness of the chiral mesoporous silica was estimated by counting characteristic morphologies from 500 randomly chosen rods in SEM images; the enantiomeric excess ($ee = [(L-R)/(L+R)] \times 100\%$) was accordingly calculated to be 33% for this CMCM-41.

Figure 6.1 VCD spectra of CMCM-41 synthesized by using previous and optimized method.

Usually, optically pure chiral surfactants or chiral dopants do not necessarily lead to the chiral silica nanoparticles with pure handedness [2, 6]. The formation of helical mesostructured silica was also anticipated from an entropy-driven model for understanding helical conformation of long molecular chains in crowded environment [7]. Therefore, the main hindrance for preparing enantiopure mesoporous silica may be ascribable to the competition between the directing effect of chiral inducer and thermodynamic driving force. The nanoscale pore

structure of CMCM-41 was characterized using TEM, as shown in Figure 6.2c and d. A typical micrograph exhibits meso-channels of ca. 3 nm in diameter. Nonetheless, fringes of some rod-like CMCM-41 corresponding to the inter-planar spacing [2, 6] are not observable in the TEM images. This may be due to the fact that the rod length is too short to discern the twisted arrangement of nano-channels regarding the significantly long helical pitch. The missing of fringes because of long pitch and short rod length was also reported by Han et al. [7]. Another possibility is that other than helical channels, the chirality of this CMCM-41 material depends on the chiral entities on a molecular level on the pore wall surfaces. The twisted hexagonal morphology of CMCM-41 particles can be attributed to the crystallization of tortured silica building blocks.

Figure 6.2 SEM micrographs of CMCM-41 (a) with low magnification, (b) with high magnification. TEM micrographs of CMCM-41 (c) with low magnification, (d) with high magnification.

The low-angle XRD pattern and nitrogen adsorption-desorption isotherms of CMCM-41 after solvent extraction are shown in Figure 6.3. These results confirm that CMCM-41 possesses a highly ordered hexagonal mesostructure and a narrow pore size distribution. The pore diameter, BET surface area and pore volume are 2.6 nm, $1047 \text{ m}^2 \text{ g}^{-1}$ and $1.9 \text{ cm}^3 \text{ g}^{-1}$, respectively. The CMCM-41 is compared with the conventional achiral MCM-41 synthesized in the absence of chiral cobalt complex, no pore enlargement is observed for CMCM-41 due to the low content of chiral cobalt complex (see Figure 6.3c).

Figure 6.3 (a) XRD pattern and (b) nitrogen adsorption-desorption isotherm of CMCM-41; (c) pore size distributions of solvent extracted MCM-41 and CMCM-41.

The UV-vis spectra of both as-synthesized and solvent-extracted CMCM-41 are shown in Figure 6.4a. The absorbance at 350 nm characteristic for d-d transition of cobalt complex [8] evidences the involvement of the chiral cobalt complex in the

synthesis of CMCM-41. All the absorbencies contributed by chiral cobalt complex vanish after solvent extraction, suggesting the complete removal of CTAB template and chiral cobalt complex. In addition, the peaks assigned to N-H and C-H stretching vibrations become invisible after the solvent extraction in the IR spectra, as seen in Figure 6.4b, which further proves the chiral cobalt complex and surfactants have been successfully taken away from the CMCM-41 channels [9, 10].

Figure 6.4 (a) UV-vis spectra and (b) IR spectra of as-synthesized and extracted CMCM-41.

To validate the local chirality in the mesoporous channels of CMCM-41, the enantioselective adsorption of racemic D, L-valine in water solution was studied using the extracted CMCM-41. The optical activity of the solution as a function of incubation time was measured using circular dichroism (CD) spectroscopy. Aqueous solution of 5 mL of the racemic valine (300 mmol/L) and 0.01 g CMCM-41 (after surfactant and chiral cobalt complex extraction) were mixed under vigorous stirring.

Optical activity of the solution was probed as a function of time. Every 2 h, 0.2 mL of solution was taken out and diluted with 1.0 mL deionized water for CD spectroscopy measurement. As shown in Figure 6.5a, the absorbance at 210 nm increases with time, implying that D-enantiomers are enriched in solution [1], due to the selective adsorption of L-enantiomers onto CMCM-41. Adsorption kinetics of pure L- and D-valine were also studied. To determine the adsorbing rates of different enantiomers, 0.05 g of pure L-valine (or D-valine) was dissolved in 20 mL of water followed by adding 0.02 g of template-free CMCM-41. The mixture was magnetically stirred under ambient conditions. The concentration of L-valine (or D-valine) was measured by UV spectroscopy (absorption at 210 nm). Both enantiomers can be adsorbed by CMCM-41 as shown in Figure 6.5c. Nevertheless, the adsorption rate of L-enantiomers is apparently higher than that of D-enantiomers and the maximum amount of L-valine adsorbed is larger than that of D-valine by a factor of 1.3, evidencing the enrichment of D-valine in the aqueous solution, which is consistent with the CD measurement. In contrast, achiral MCM-41 synthesized in the absence of chiral cobalt complex shows the same adsorption coefficients for two enantiomers (see Figure 6.5b). As mentioned above, the chiral cobalt complex has been completely removed from the extracted CMCM-41 sample as confirmed by IR and UV-vis measurements. These findings demonstrate the enantioselectivity of this CMCM-41 for an enantiomeric pair, and the existence of local chiral chemical environment inside the mesoporous channels. It is noteworthy that as with metoprolol we used previously, the molecular structure of valine is also distinct with that of CCC, which may suggest that our CMCM-41 possesses the general enantioselectivity just like the amorphous

chiral silica synthesized by Fireman-Shoresh et al. [4]. The separation of rest seven pure enantiomers of $[\text{Co}(+)(\text{chxn})_3]\text{I}_3$ is not straightforward [11]. In this study, we have only attempted to employ a mixture of the rest seven isomers of $[\text{Co}(+)(\text{chxn})_3]\text{I}_3$ as the co-template to synthesize mesoporous silica. As shown in Figure 6.5d, the adsorption profiles of pure L- and D-valine are almost identical considering the experimental error, suggesting the lack of enantioselective discrimination ability in this material.

Figure 6.5 CD spectra of a racemic valine solution with (a) solvent extracted CMCM-41, and (c) achiral MCM-41 as a function of time: a) 0, b) 4, c) 6, d) 8 and e) 10 h; (b) and (c) adsorbing profiles of pure D- and L-valine on CMCM-41 and MCM-41, respectively.

6.2 Tentative chirality transfer mechanism

Figure 6.6 VCD and IR spectra of as-synthesized CMCM-41, (a and c) between 850 and 1400 cm^{-1} (b and d) between 2800 and 3000 cm^{-1} .

In order to elucidate the chirality transfer steps, the local chirality of this mesoporous silica along with the micelle template and chiral co-template is characterized by VCD spectroscopy. Figure 6.6a shows the VCD and IR spectra of the as-synthesized CMCM-41. Three strong bands at 962, 1080 and 1217 cm^{-1} of VCD spectrum correspond well with IR results, which are assigned to the Si-O asymmetric vibration [12]. After removing templates, the VCD signal intensities decrease to some

extent, as shown in Figure 6.7, which may be contributed by the condensation of Si-OH groups and restructuring of SiO₄ tetrahedrons caused by repeated solvent extraction in hot ethanol.

Figure 6.7 VCD spectra of as-synthesized and template free CMCM-41.

Control experiments show no VCD response in the mid-IR region (Figure 6.6c) from silica source, surfactant, cobalt complex, and achiral silica synthesized in absence of chiral cobalt complex. It is suggested that the chiral Si-O conformations may be formed during the synthesis of mesoporous silica, which would afford the local chiral environment (chiral motif) on the pore wall surface. Furthermore, the VCD spectrum of as-synthesized CMCM-41 also shows two signals at 2851 and 2918 cm⁻¹, which can be correlated to the IR bands assigned to C-H asymmetric vibrations of -CH₃ and -CH₂-, respectively (Figure 6.6b) [13, 14]. These peaks are absent in the VCD spectrum of template free CMCM-41 (see Figure 6.7). In contrast, both

surfactant and cobalt complex do not exhibit analogous signals presenting in as-synthesized CMCM-41 (Figure 6.6d). It has been previously established that the propellane-like structure of the cobalt complex attained under similar reaction conditions because of its rigidity [15]. Consequently, it is highly probable that the rigid chiral complex with planar chirality induces the formation of a chiral aggregation in the synthesis of CMCM-41, which contributes to the VCD signals of hydrocarbon (as shown in Scheme 6.1a).

Scheme 6.1 (a) Chiral silica building blocks induced by chiral aggregations in hexagonal meso-phase. (b) Lamellar mesoporous silica formed at high CCC/Na₂SiO₃ molar ratio; (c) Conventional MCM-50 templated by surfactants only; (d) Lamellar mesoporous silica formed at high EA/Na₂SiO₃ molar ratio.

To further investigate the interaction between CCC and CTAB, zeta potentials of micelle template as a function of CCC/CTAB molar ratio was measured, as depicted in Figure 6.8. The fact that zeta potentials of CTAB micelles gradually decrease upon adding chiral cobalt complex implies the diminishing charge intensity of micelle template surface [16]. It is unreasonable to suggest that a cation (Λ -[Co(+)(chxn)₃])³⁺ or salt (CCC) locates deep inside the hydrophobic core of micelles. In addition, the zeta potential of micelle surfaces should maintain constant if the cobalt complex is mainly present inside the micelle. We postulate that the chiral cobalt complex may intercalate in the sub-surface of micelles, i.e., the hydrocarbon-water interface of micelle which intervenes between water and the organic phases inside the core of micelle [17], as seen in Figure 6.8 (inset), due to the fact that Λ -[Co(+)(chxn)₃] has both hydrophobic (cyclohexane rings) and hydrophilic (amino groups and cobalt ion) components. Because the Co³⁺ is coordinated to three trans-1,2-cyclohexanediamine (chxn) ligands. Although this cobalt complex is highly positively charged, the iodine counter ion may compensate for the positive charge on the micelle surface. Additionally, the cross sectional area of this cobalt complex is approximately 6 times larger than that of CTAB head group (which is equivalent to the area taking place by 4 CH₂, 4×0.04 nm² = 0.16 nm²) [18]. Therefore, charge density of this cobalt complex is halved in comparison with the head group of CTAB and the imbedded CCC should contribute to the decreasing zeta potential of micelles.

Figure 6.8 Zeta potentials of surfactant micelle as a function of CCC/CTAB molar ratio, inset: proposed interaction between chiral cobalt complex, surfactant micelle, and silica precursor.

It is generally accepted that salt ions have a remarkable effect on the electrostatic interactions between the silica source and surfactant template [19]. In our synthesis, the intensity of VCD signals decreases with increasing the KCl/ Na₂SiO₃ molar ratio (Figure 6.9). These results suggest that the formation of CMCM-41 is based on the self-assembly of micelle template containing chiral aggregation and surrounding silica precursors by strong electrostatic interactions. The decreased intensity of VCD signals (weak chiral confirmation of chiral mesoporous silica) in the presence of KCl salts corroborates the mechanism of chirality transfer from the chiral aggregation composed of chiral cobalt complex and adjacent surfactants to silica precursor based on electrostatic interactions.

Figure 6.9 VCD spectra of as-synthesized CMCM-41 with various KCl/Si molar ratios, inset: attenuation of electrostatic interaction between template and silica precursor in the presence of KCl.

Based on the above findings, we propose that the propellane-like chiral cobalt complex may twist surfactant head groups nearby without disturbing the macroscopic arrangement of micelles; the resulting asymmetrically deformed aggregation containing chiral cobalt complex and surfactants would subsequently afford a chiral template for the synthesis of mesoporous silica with microscopic chiral environment on the pore wall surfaces. The chirality transferring from chiral aggregations to silica largely relies on the electrostatic interactions. It is noteworthy the local asymmetric distortion of surfactants is induced by rigid metal complex with planar chirality and strong stereospecific effect, which is distinct from liquid crystal phase transformation

of micelles arising from adding soft or small chiral dopants with a stereogenic carbon and weak stereospecific effect, where the alignment of surfactants has been altered completely, leading to the formation of macroscopic chiral meso-phase [2, 20].

6.3 Effects of CCC

It is speculated that CCC as a co-template may have significant influence in the formation of CMCM-41. The XRD patterns of CMCM-41 with different CCC/Na₂SiO₃ molar ratios are shown in Figure 6.10 (left). The optimal synthesis condition for CMCM-41 structure occurs using a molar ratio of 0.06, as evidenced by a strong (100) diffraction and two high-angle diffraction peaks. Remarkably weak diffraction peaks are observed when the molar ratio is as low as 0.03, implying a poorly ordered mesostructure. Interestingly, as the molar ratio increases to 0.09, the silica sample exhibits a low-intensity (100) diffraction peak from hexagonal structure along with two diffraction peaks indexed as (100) and (200) reflections for lamellar structure at high angle (see Figure 6.10 (left, c)), implying that the transformation from hexagonal pore arrangement to a layered structure occurs [21]. The pure layered phase is obtained when the molar ratio increases to 0.12. SEM images (Figure 6.10 (right)) reveal the morphologies of these silica particles synthesized with different CCC/Na₂SiO₃ molar ratios. As seen in Figure 6.10 (right, a), the resulting particles with low molar ratio of 0.03 have twisted bean-like morphology with diameter ranging from 0.5-0.8 μm . When the molar ratio increases to 0.06, particles with the helical hexagonal rod-like morphologies are formed as depicted in Figure 6.10 (right, b). With further increasing the molar ratio, the product with layered plate-like morphology appears gradually as shown in Figure 6.10 (right, c and d), which

coincides with the XRD results. The formation of lamellar mesoporous silica is also consistent with the zeta potential measurements. Adding an excess amount of CCC may facilitate the insertion of cobalt complex into micelle and reduce the effective area of CTAB head group due to the smaller electrostatic density of micelle surface, leading to the phase transformation from hexagonal to lamellar structure [21].

Figure 6.10 XRD patterns (left) and SEM micrographs (right) of CMCM-41 synthesized with various CCC/Na₂SiO₃ molar ratios (a) 0.03, (b) 0.06, (c) 0.09, (d) 0.12.

The d -spacing of lamellar structure ($d_{100}=2.6$ nm) in this study is smaller than that of conventional MCM-50 type mesoporous silicas ($d_{100}=3.6$ nm) which were synthesized using only CTAB as template and sodium silicate as silica source [22]. The mesopore size is mainly determined by the molecular dimension of templates (usually the hydrocarbon chain length of surfactants) [23]. The significant change of d_{100} spacing in this study should not be caused by the variation of preparing factors such as pH value, reaction time and silica source, especially in the preparation of mesoporous silica templated by ionic surfactants [24]. We proposed

another self-assemble for Λ -[Co(+)(chxn)₃]³⁺ and surfactants due to the addition of a large amount of chiral cobalt complex, as illustrated in Scheme 6.1b. The silica walls of chiral lamellar mesoporous silica are segregated by one layer of surfactants and one layer of Λ -[Co(+)(chxn)₃]³⁺, leading to a smaller d_{100} space compared to that of conventional MCM-50 in which the silica walls are embraced by two layer of surfactants (see Scheme 6.1 c).

Interestingly, high CCC/Na₂SiO₃ molar ratio does not necessarily lead to the formation of mesoporous silica with remarkable chirality. On the contrary, the intensity of silica VCD signal for lamellar mesoporous silica is essentially weaker than that of hexagonal CMCM-41, as shown in Figure 6.11. VCD characterization is an extension of CD measurement to the infrared region. The signal of VCD can only be associated with the asymmetric vibration of chemical bonds, rather than macroscopic chirality such as the helical mesostructure. These results suggest that the chirality of CCC cannot be directly transferred to silica motif, and the chirality transfer is weakened due to the formation of lamellar meso-phase, which is ascribed to the change of self-assembly of Λ -[Co(+)(chxn)₃] and adjacent surfactants, i.e., the formation of a new type of chiral aggregation, as a result of phase transformation from hexagonal to lamellar (as shown in Scheme 6.1a and b). The new chiral aggregations in lamellar phase can be evidenced by the changes of hydrocarbon signals in a high wavelength number region (2800-3000 cm⁻¹) including the disappearance of -CH₃ signal and the reverse of -CH₂- signal. Similar to the conventional MCM-50, any attempts (such as solvent extraction and calcination) to remove templates from lamellar mesoporous silica result in the collapse of the mesostructure and the

formation of amorphous silica. The chiral signals completely diminish for the amorphous silica as shown in Figure 6.11, suggesting that the weak chirality of lamellar silica is vulnerable to the repeated extraction processes using hot ethanol.

Figure 6.11 VCD spectra of as-synthesized CMCM-41, as-synthesized lamellar mesoporous silica and amorphous silica obtained by removal templates from chiral lamellar silica.

6.4 Effects of EA

Similar phase transformation from hexagonal to lamellar structure is also observed when the amount of EA in the synthesis solution is varied. The XRD patterns of CMCM-41 with different EA/Na₂SiO₃ molar ratios are shown in Figure 6.12 (left). Three well-resolved diffraction peaks indexed as (100), (110), and (200) reflections imply highly ordered hexagonal mesostructure occurring at the optimized EA/Na₂SiO₃ molar ratio of 6. Low content of EA leads to a poorly

ordered mesostructure, which indicates the poor self-assembly of silica oligomers and CTAB into a hexagonal mesostructure due to the hydrolysis of insufficient EA [25]. Increasing the molar ratio results in the phase transformation from hexagonal pore arrangement to a layered structure during the synthesis of CMCM-41. The morphologies are displayed in Figure 6.12 (right). The resulting particles afford bean-like, hexagonal rod-like, and layered plate-like morphologies as the molar ratio gradually increases. As the lamellar structure of mesoporous silica synthesized at high EA/Na₂SiO₃ molar ratio is remarkably similar as compared to that of meso-silica synthesized using high CCC/Na₂SiO₃ molar ratio, one can conclude that the excess hydrolysis of EA may enhance the embedding of Λ -[Co(+)(chxn)₃] into CTAB micelles.

Figure 6.12 XRD patterns (left) and SEM micrographs (right) of CMCM-41 synthesized with various EA/Na₂SiO₃ molar ratios (a) 3, (b) 6, (c) 9, (d) 12.

For the lamellar meso-silica formed at high EA/Na₂SiO₃ molar ratio, we speculate a synergic effect of EA in the incorporation of CCC into CTAB micelles. In this synthesis, EA was hydrolyzed to ethanol and acetic acid which would lower the pH

value and initiate the hydrolyzation and polymerization of silicates [25]. It has been reported that neutral hexanol molecules can insert into CTAB micelles and reduce the area per hydrophilic group occupied (a_0) at the surface of micelle [26], ethanol may play the same role as that of hexanol; negatively charged acetate anions may interact with positively charged CTAB head groups to neutralize the charges on the surface of micelles [16]. Thus, the products of EA hydrolysis may promote the intercalation of cobalt complexes by minimizing the charge density on the surface of micelles and decreasing the electrostatic repulsion between micelles and $\Lambda\text{-[Co(+) (chxn)}_3\text{]}^{3+}$ (see Scheme 6.1d). The interactions between surfactants and EA hydrolysis products hinder the chirality transferring from asymmetric aggregation to silica building blocks. As shown in the VCD spectrum of lamellar chiral silica prepared at the highest EA/Na₂SiO₃ molar ratio (Figure 6.13), the signals of chiral silica almost disappear and the peaks assigned to hydrocarbons are also weakened. This observation is consistent with the blocked chirality transfer due to the addition of salt ions (KCl). However, the signal of -CH_3 can be detected, which may be contributed by the interaction between chiral complex and -CH_3 moieties of ethanol or acetic acid.

Figure 6.13 VCD spectra of as-synthesized CMCM-41 and as-synthesized lamellar mesoporous silica at high EA/Na₂SiO₃ molar ratio.

6.5 Summary

In summary, a CMCM-41 with twisted particle morphology was synthesized using achiral CTAB as template and a chiral metal complex CCC as the co-template. The chirality of CMCM-41 was characterized by enantioselective adsorption of racemic valine. The local chiral conformation at a molecule level and the chirality transfer mechanism were investigated by VCD spectroscopy. The CMCM-41 silica channels exhibited local chiral characteristics which can be explained by the existence of the asymmetrically distorted SiO₄ tetrahedrons. It is proposed that the rigid cobalt complex with planar chirality can incorporate into the sub-layer of micelle and induce the distortion of adjacent surfactants to afford the formation of a chiral aggregation which subsequently transfers the chirality to

the silica motif of CMCM-41 via electrostatic interaction. Increasing the concentration of chiral cobalt complex or EA leads to the meso-phase transformation from hexagonal to lamellar which may impair the chirality transfer. This study may contribute to the synthesis of mesoporous silica materials with chiral entities at molecular level and understanding the chirality transfer steps from organic template with inherent chirality to inorganic building blocks. Further investigations into the synthesis of chiral nanoporous materials using other chiral metal complexes are considered. This work has been published in Journal of Physical Chemistry (Guo et al. Journal of Physical Chemistry C, 2010, 114(34), 14353-14361), reuse in this chapter is under the permission of Amecial Chemical Society publishing group.

List of abbreviations

BET	Brunauer-Emmett-Teller
CCC	Chiral Cobalt Complex
CD	Circular Dichroism
CMS	Chiral Mesoporous Silica
CTAB	Hexadecyltrimethylammonium Bromide
EA	Ethyl Acetate
IR	Infrared Spectroscopy
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscopy
UV	Ultraviolet
UV-vis	UV-visible
VCD	Vibrational Circular Dichroism
XRD	X-Rays Diffraction

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Chapter 7 Immobilization of Monodentate Phosphoramidite Ligand based Chiral Catalysts and Their Applications in Asymmetric Hydrogenation of Dimethyl Itaconate

In Chapter 5, Pt nanoparticles supported on chiral mesoporous silica were employed as heterogeneous catalysts for asymmetric hydrogenation of dimethyl itaconate. The low enantio-bias was attributed to the weak asymmetric induction capability of chiral active sites, i.e., chiral moieties on the pore wall surfaces of mesoporous silica. Therefore, at the current stage of studies on chiral catalysts, the immobilization of homogeneous chiral catalysts may be an applicable way to prepare heterogeneous chiral catalysts with excellent catalytic performances [1], which will be of the focus of this chapter.

Various chiral catalysts with high catalytic activity and enantioselectivity have been developed [2]. For a long period of time, bidentate ligands which have more than one atom coordinating with active metal center are preferred due to their coordinating configuration and symmetry [3]. It was believed that these features of bidentate ligands were essential for an effective asymmetric catalyst. Nevertheless, a revival of study on monodentate phosphorous ligands (MPL) has been taking place because novel enantio-pure phosphoramidite ligands showed excellent properties in enantioselective hydrogenation and conjugate addition [4]. Different from metal complexes composed of bidentate ligands, monodentate phosphoramidite complex consists of two isolated monodentate ligands; each of them has only one atom coordinating with the metal center. The unique coordination scheme of MPL based metal complex allows the formation of catalysts with mono- [4] or hetero-coordinated

[5] configurations in addition to the homo-coordination, as illustrated in Scheme 7.1a and b. Mono-coordinated complexes have been reported highly active in homogeneous asymmetric reactions [4]. Furthermore, mixture of different MPL (hetero-coordinated complex) may improve the enantio-excess (*ee*) value tremendously [6]. Nevertheless, under homogeneous condition, it is unlikely to prepared mono- or hetero-complex in a pure form due to rapid ligand exchange [7]. We propose a novel method to synthesize mono-coordinated asymmetric catalyst, as shown in Scheme 7.1c. One MPL is firstly immobilized on the support surfaces, which can coordinate with metal center to form the mono-coordinated metal complex. Subsequently, a controlled coordination of a second MPL with metal center is performed which will afford either homo-coordinated asymmetric metal complex depending on the selection of the second MPL.

Scheme 7.1 Formation of homo-, hetero- and mono-coordinated metal complexes in solution (a, b) and on a support (c). M and L represent the metal and ligand, respectively.

Many works have been reported on the methods of anchoring homogeneous catalysts on carriers, such as covalent bonding [8], ion interaction [9], and steric confinement [1]. Although covalent bonding and entrapment may effectively minimize the leaking of catalytically active components, the catalytic properties of immobilized catalysts may be different from their homogeneous counterpart due to the alteration of ligand structure or steric effect imposed by support pore wall surfaces [1]. It is convenient to immobilize a free metal complex via ion interaction, which can retain the properties of the homogeneous catalyst to a large extent. Nevertheless, the electrostatic interaction usually is not strong enough to prevent the loss of catalysts during recycle.

MPL—Rh complexes have been successfully immobilized on alumina doped silica via electrostatic interaction between the metal complex and the basic sites on the support [10]. The molecular structure of MPL can be modified as a monomer, and thus copolymerization of the modified MPL and styrene resulted in a heterogeneous catalyst in a form of polymer [8]. Although some loss in selectivity was observed, these polymerized catalysts showed a reasonable *ee* value (up to 80%) [8]. The recycle of this asymmetric catalyst was achieved by adding another solvent (methanol) to precipitate the polymerized catalyst.

In this chapter, we will try to anchor the synthesized MPL on the surfaces of rigid supports—mesoporous silica and carbon nanotubes via covalent bond and electronic interaction, respectively, which allows controlling the coordination manner of MPL—metal complex in terms of ligand/metal ratio, in which mono-complex can be formed (See Scheme 7.1c). To compare the catalytic performances of immobilized mono- and

homo-complex, it may help to understand the intrinsic property of monodentate phosphoramidite-rhodium based complexes.

7.1 Synthesis of monodentate phosphoramidite ligand

Monodentate phosphoramidite is one of the frequently adopted MPL. Its molecular structure is usually composed by a bulky chiral backbone (from enantiopure BINOL) and an amine group (see Scheme 7.2). These two parts are connected by a P-N single bond, only phosphorous will be able to coordinate with metal cation (e.g., Rh). As shown in Scheme 7.2, the synthesis procedures of MPL include two steps catalyzed by an organic base triethylamine (NEt_3). Firstly, phosphorous trichloride (PCl_3) reacts with BINOL to give rise an intermediate product (BPC), followed by adding the amine group, which connects with the chiral backbone via P-N bond. The leaving Cl will be precipitated in form of alkylammonium chloride ($\text{NEt}_3 \cdot \text{HCl}$). Although the synthesis method is simple, both the reaction and purification steps are conducted in the inert atmosphere, as MPL is sensitive to moisture and oxygen in air [11].

Scheme 7.2 Synthesis procedures and molecular structure of target MPL ligand (BPEAn).

Our target MPL (denoted as BPEAn, as shown in Scheme 7.2) is synthesized by using BINOL and an amine (N-ethylaniline) as building blocks, which are bridged with a phosphorous atom. The reason of choosing N-ethylaniline as the precursor of amine moiety is due to our proposed strategy for immobilizing ligand. Immobilization of BINOL on mesoporous silica has been reported. Usually the naphthyl moiety of BINOL is modified by introducing a silanol arm which will react with the silanol groups on the surface of silica support to give rise a Si-O-Si bond (see Scheme 7.3) [12, 13]. The advantage of this approach is that the connecting part (Si-O-Si) between ligand molecule (BINOL) and support is far from the active center (metal ion), which may largely retain the properties of immobilized catalyst in homogeneous state [13]. Nevertheless, as shown in Scheme 7.3, the immobilization procedure is complicated involving several steps. Therefore, loss of starting precursors and waste of solvent are inevitable during each preparation or purification step. For MPL, the immobilization of amine group can be easily achieved by grafting the commercial organic silicate compound containing amino group (such as AnPTMS as shown in Scheme 7.2) on the surface of silica support, which is similar to the step “f” in Scheme 7.3. The anchored MPL may be obtained by introducing BPC to react with immobilized amine (detailed immobilization strategy will be discussed in Section 7.2). As the catalytic performances of immobilized mono- and hetero-complex will be compared, it is necessary to minimize the difference between immobilized ligand and free ligand, and this is the primary reason why the molecular structure of BPEAn is designed.

Scheme 7.3 The synthetic routes for immobilizing BINOL on mesoporous silica by tethering the chiral backbone of BINOL with silanol groups on support surfaces [12].

Both the intermediate product (PBC) and final ligand (BPEAn) were characterized by ^1H and ^{31}P NMR. As shown in Figure 7.1a, peaks between 7 and 8 ppm can be assigned to the resonance of hydrogen atoms of the chiral backbone. The peak for hydrogen of hydroxyl groups of BINOL are absent in the ^1H NMR spectrum of BPC, suggesting that the two O-H bonds have been replaced by two O-P bonds (see Scheme 7.2). The chemical shift of phosphorous in BPC is 178 ppm (see Figure 7.1 b) which is consistent with the value reported by others [14]. After bonding amine part with BPC, the new peaks detected in the ^1H NMR spectrum of BPEAn can be attributed to the

resonance of hydrogen atoms of the phenyl and ethyl groups (marked by arrows in Figure 7.1c). The phosphorous chemical shift of BPEAn ($\delta = 143$) is also in the range of phosphoramidite compounds (see Figure 7.1d) [15]. Only one chemical shift peak can be found in each ^{31}P NMR spectrum, suggesting that the phosphorous impurities such as starting materials and oxidized by-products are absent in the purified products. The yields of BPC and BPEAn are 92% and 60%, respectively.

Figure 7.1 ^1H (left) and ^{31}P (right) NMR spectra of BPC and BPEAn.

7.2 Immobilization of monodentate phosphoramidite ligand on SBA-15

Mesoporous silica—SBA-15 was chosen as support not only because of its large accessible surface area, but also its large pore size (usually 6-8 nm) which enables accommodating bulky molecules inside the channels [16]. As shown in Scheme 7.4, the immobilization of MPL—BPEAn was carried out by modifying SBA-15 in three

consecutive steps. Firstly, amino groups were bonded to the support by grafting AnPTMS on SBA-15 surfaces; Secondly, the residual silanol groups were capped by methyl groups before adding BPC to prevent reaction taking place between BPC and silanol groups; Subsequently, BPC was introduced to react with the amino groups, leading to the formation of immobilized MPL. Based on element analysis (EA) results, the weight percentage of phosphorus in the final powder (denoted as PMAAn-SBA-15) is 0.9 wt.%. The preparation of immobilized mono-complex was attempted by adding equal mole of Rh precursors in solution, while the homo-complex was obtained by introducing equal mole of free ligand (BPEAn) after sufficiently incubation of the immobilized ligand in Rh solution.

Scheme 7.4 The strategy for immobilizing BPEAn based on the modification of SBA-15 silica (step 1 to 3) and *in situ* formation of heterogenized mono- or homo-complex.

The as-synthesized and modified SBA-15 silicas are characterized by XRD and nitrogen physisorption measurements. As shown in Figure 7.2 left, three well-resolved diffraction peaks, indexed as (100), (110), and (200) reflections of 2d hexagonal space group (p6mm, $a=10.2$ nm) can be clearly discerned in the XRD pattern of as-synthesized SBA-15, implying the successful synthesis of SBA-15 with highly ordered mesostructure [17]. These diffraction peaks are present in all XRD patterns of modified SBA-15, suggesting that the ordered mesoporous structures are retained after several steps of modification.

Figure 7.2 XRD patterns (left) and nitrogen physisorption isotherms (right) of SBA-15 and modified SBA-15.

As expected, modification of SBA-15 reduces the surface area, pore volume and pore size due to the introduction of organic moieties in mesopores (see Figure 7.2 (right) and Table 7.1). Two sharp desorption steps can be discerned for the desorption

branch of PMA_n-SBA-15, which indicates the existence of pores with two mean diameters. Different from the previous modification steps, bulky groups will be attached onto SBA-15 surfaces in step 3, thus the transport resistance for the large molecules during this particular modification step should be large and most of the moieties prefer staying in the entrance of pores instead of the pore wall surfaces, resulting in the formation of this bimodal pore size distribution. The attachment of organic functional groups on SBA-15 surfaces is also evidenced by EA, as shown in Table 7.1. Both carbon and hydrogen contents increase after bonding methyl groups (MA_n-SBA-15) and BPC (PMA_n-SBA-15) onto An-SBA-15, while the weight percentage of nitrogen slightly decreases due to the grafting of new organic moieties. Nevertheless, the mole ratio of phosphorous to nitrogen is less than 1 (around 0.45), which may be due to the difficulty for bulky BPC to react with the amino groups locating at the inner pore wall surfaces of SBA-15.

Table 7.1 Porous parameters and EA results of as-synthesized and modified SBA-15.

Samples	Pore size ^a	Specific	Pore volume	C	H	N
	(nm)	surface area	^b	(wt.%)	(wt.%)	(wt.%)
		(m ² /g)	(cm ³ /g)			
SBA-15	5.8	974	1.44	--	--	--
An-SBA-15	5.0	472	0.91	9.4	1.8	1.07
MAn-SBA-15	5.1	378	0.55	10.5	2.1	0.96
PMan-SBA-15	3.9	329	0.47	15.8	3.1	0.91

^a obtained from desorption branches using BJH method^b determined as the total adsorbed volume at $P/P_0 \approx 0.99$.

Figure 7.3 *in situ* FTIR spectra of pristine and modified SBA-15.

To further substantiate the anchoring of organic moieties on SBA-15 pore wall surfaces, *in situ* FTIR and diffuse reflectance UV-vis-NIR spectroscopic measurements were conducted. The *in situ* FTIR technique eliminates the influences of moisture adsorbed on samples during signal collection (refer to Chapter 3 for experimental details) because the IR absorption of water overlaps with the silanol groups on SBA-15 [18]. Both absorptions of organic moieties and diminishing of silanol groups are detected in the FTIR spectra of pristine and modified SBA-15 as shown in Figure 7.3. For modified SBA-15, absorption bands at 2900, 1455 cm^{-1} are contributed by the vibration of C-H bonds and absorption at around 1380 cm^{-1} can be assigned to the deformation vibration of CH_3 groups [13, 19]. The later absorption can also be observed in the spectrum of An-SBA-15, which may be due to the residual unreacted $\text{CH}_3\text{O}-$ moieties of silane (AnPTMS). After grafting methyl groups (MAn-SBA-15), the broad band around 3450 cm^{-1} disappears, implying the successful capping of residual silanol groups on An-SBA-15 [18]. New peaks at 1500 and 1600

cm^{-1} for PMAAn-SBA-15 are attributed to the vibration of benzene rings [20]. The remarkable increase in the signal at around 1660 cm^{-1} may also be caused by introducing naphthyl moieties onto SBA-15 because the signal of benzene rings and silica overlap in this range [20].

Diffuse reflectance UV-vis-NIR spectroscopy is another sensitive measurement to detect the amino groups grafted on support surfaces [18]. As shown in Figure 7.4, the absorption bands at 1900 and 1400 nm are assigned to the vibrations of silanol groups and adsorbed water, respectively [18]. These signals decrease dramatically after replacing silanol groups by methyl groups, as result of the enhanced hydrophobicity of MAAn-SBA-15. The peaks at 1530 nm in the modified SBA-15 spectra can be attributed to the stretching vibration of amino groups [18]. The reflection bands around 1675 nm are related with the vibration of CH_2 in the propyl chain between amino group and support [18]. These observations further substantiate the successful modification of SBA-15 surfaces. Due to the limit of experimental condition, UV-vis-NIR spectroscopic measurement was not carried out for PMAAn-SBA-15 which is sensitive to air.

Figure 7.4 Diffuse reflectance UV-vis-NIR spectra of pristine and modified SBA-15.

7.3 *Asymmetric hydrogenation of dimethyl itaconate*

Asymmetric hydrogenation of dimethyl itaconate (see Scheme 7.5) was carried out over BPEAn based homogeneous catalyst and heterogeneous catalysts. The results are summarized in Table 7.2. Decent enantio-excess value ($ee = 80.5\%$) was obtained over the homogeneous catalysts (see Table 7.2 entry 1 and 2). Similar with the reported results in literature, both activity and selectivity remain constant when changing the ligand (L)/metal (M) ratio from 1:1 (BPEAn-Rh) to 2:1 (2BPEAn-Rh). Nevertheless, under the homogeneous reaction conditions, the homo-complex and mono-complex may exist simultaneously even when the L/M ratio is 1, due to the ligand exchange between different complexes. Thus, it is difficult to identify the role played by mono-complex.

Scheme 7.5 Asymmetric hydrogenation of dimethyl itaconate.

The immobilized mono-complexes (denoted as BPEAn-Rh/SBA-15) were prepared by mixing PMAAn-SBA-15 with metal precursor $\text{Rh}(\text{COD})_2\text{BF}_4$, and subsequently incubating BPEAn-Rh/SBA-15 and BPEAn in CH_2Cl_2 , leading to the formation of immobilized homo-complexes (denoted as BPEAn $\times$ 2-Rh/SBA-15). A remarkable decrease in the conversion is observed over the immobilized mono-complexes (see entry 3) along with zero enantio-bias. This may suggest that the anchored mono-complex (see Scheme 7.4 step 4) is lack of chiral discrimination capability in its immobilized configuration. The low conversion may due to the transport hindrance inside the SBA-15 mesopores, which may be overstated by introducing bulky ligand-metal clusters. It may also explain the further lower conversion obtained over BPEAn $\times$ 2-Rh/SBA-15 in which the size of metal complex should be much larger as two ligands are coordinating with one metal center.

Table 7.2 Asymmetric hydrogenation of dimethyl itaconate over Rh-MPL homogeneous and heterogeneous catalysts.

Entry	Catalysts	Conversion (%) ^a	<i>ee</i> (%) ^b
1	BPEAn-Rh	100	80.5
2	BPEAn×2-Rh	100	80.5
3	BPEAn-Rh/SBA-15	17.6	0.0
4	BPEAn×2-Rh/SBA-15	5.1	-5.0
5	BPEAn×2-Rh/SBA-15 (R) ^c	5.0	-4.8
6	BPEAn-Rh/CNTs	100	43.0
7	BPEAn×2-Rh/CNTs	100	73.1
8	BPEAn×2-Rh/CNTs (R) ^c	44.1	10.1

^a Determined by gas chromatograph ;

^b $ee = (R-S) \times 100\% / (R+S)$ (see Chapter 3 Equation 3.4);

^c Hydrogenation reaction using a recycled catalyst.

Interestingly, an opposite enantio-selectivity of immobilized homo-complex is observed (see entry 4), although the *ee* value is still low. According to the “unsaturated pathway” of asymmetric hydrogenation catalyzed by Rh, the prochiral substrate can coordinate with the active metal center from two different enantio-faces, resulting in two diastereomeric catalyst-substrate complexes [21]. Subsequent hydrogenation of these diastereomers will give rise to two opposite enantiomers. The coordination mode of catalyst-substrate complexes may be determined by the bulkiness of the ligands or different solvents [22, 23]. In fact, opposite enantioselectivity has been found in homogeneous catalytic system by attaching a

bulky organic group on ligand [22] as well as in heterogeneous catalytic system by changing solvent [23]. Opposite enantio-selection caused by heterogenized homogeneous catalysts was also reported by Wan et al., in which SBA-15 and MCM-41 were employed as support materials [24]. It was suggested that the change of enantio-selection was contributed by the adsorption of product in vicinity of the immobilized catalytically active center because the adsorbed product may act as a bulky ligand in the reaction [24]. This effect may be more pronounced if the product cannot diffuse to solution rapidly, such as in the mesoporous channels decorated by bulky organic groups. To some extent, the surface of support may also be deemed as a big bulky moiety on a molecular level once the ligand is tethered on the support. The change of ligands as a result of immobilization may affect the coordination mode of substrate (dimethyl itaconate) with catalyst, leading to opposite enantioselectivity. Recycle and reuse of the immobilized homo-complex show only slightly decrease of conversion and selectivity, suggesting the robustness of the heterogeneous catalyst prepared by anchoring ligand via covalent bond.

Covalent bonding of asymmetric catalysts on a rigid surface results in poor enantioselectivity, which may due to the altered configuration of intermediate on the surfaces during hydrogenation steps. It has been generally accepted that the chirality of final products is determined by the coordination scheme of intermediate metal complex composed by original catalyst, substrate and oxidatively added hydrogen [21]. Thus, the coordination between ligand and substrate plays a critical role in enantioselectivity [25]. Bonding ligand on a support inevitably affects the interaction between ligand and substrate, which may be responsible for the low selectivity of either

immobilized mono- or homo-complex. Furthermore, the low activity of immobilized catalysts can be attributed to the mass transport resistance inside the mesoporous channels of SBA-15 as a result of the blockage by large organic moieties. It was proposed that anchoring the homogeneous catalyst by adsorption method may preserve the catalytic properties to a large extent due to the weaker interaction between chiral centers and surfaces that may less disturbance to the asymmetric catalysts. Surface of multi-walled carbon nanotube (CNTs) can be modified by adsorbing compound with aromatic ring interacting with the graphite plane via π -stacking [26]. As BPEAn contains a large aromatic backbone and an aryl ring at amine domain, homogeneous catalysts with different L/M ratio (1:1 and 2:1) were loaded on CNTs surfaces by adsorption (refer to Chapter 3 for experimental details) and applied to the asymmetric hydrogenation of dimethyl itaconate. The results are listed in Table 7.2 (see entry 6-8). Different from immobilized catalysts supported by SBA-15 via covalent bonds, catalysts adsorbed on CNTs surfaces show activity comparable to their homogeneous counterparts (see entry 6 and 7), which may due to the highly accessible active sites adsorbed on the surface of CNTs. Nevertheless, the *ee* value of mono-complex is halved and the enantioselectivity of homo-complex also decreases after immobilizing these catalysts on CNTs surfaces. In the asymmetric hydrogenation catalyzed by heterogenized mono-complex (BPEAn-Rh/CNTs), the density of ligand on CNTs surfaces is low; it is highly possible that most of the ligands are attached to the surface of CNTs due to strong π -stacking, which may impair the chiral recognition capability of the immobilized catalyst. Therefore, the decrease of enantioselectivity of BPEAn-Rh/CNTs is more pronounced than that of immobilized homo-complex

(BPEAn $\times$ 2-Rh/CNTs). Nevertheless, the enantioselectivity of CNTs supported catalysts is better than that of metal complex anchored on SBA-15 via covalent bonds, which may due to the preservation of the catalytic properties of homogeneous counterpart. Recycle and reuse of BPEAn $\times$ 2-Rh/CNTs shows remarkable decrease in activity and enantioselectivity, implying the leaching of catalysts during the filtration and washing steps. In other words, unlike the covalent bond, the π - π interaction between BPEAn and CNTs is not strong enough to attain the active sites in this catalytic system.

7.4 Summary

A monodentate phosphoramidite ligand (BPEAn) was synthesized and immobilized on SBA-15 and CNTs surfaces via covalent bond and π - π interaction, respectively. In asymmetric hydrogenation of dimethyl itaconate, 80.5% ee at 100% conversion was obtained by using BPEAn-Rh complexes as the homogeneous catalysts, which are comparable to the reported results. Changing the ligand/metal ratio from 2 to 1 did not lead to variations of both conversion and selectivity, implying that monodentate ligand is also active in catalyzing the asymmetric reaction. However, substantially low activity and negligible enantioselectivity were found over mono-complex that was immobilized on SBA-15 surfaces, which can be attributed to the mass transfer resistance in mesopores of SBA-15 after tethering bulky functional groups as well as to the changes in the nature of immobilized ligand as a result of covalent bonding. Interestingly, an opposite enantio-selection was observed when SBA-15 supported homo-complex was employed as catalyst. The unusual phenomenon was tentatively ascribed to the adsorption of product in the vicinity of

catalytically active centers. Recycle and reuse of the homo-complex covalently bonded on SBA-15 did not lead to significant loss of activity and enantioselectivity. Improved catalytic results were obtained over CNTs supported metal complexes prepared by adsorption method. However, the interaction between catalyst and CNTs surfaces was not strong enough to prevent the leaching of active components.

List of abbreviations

AnPTMS	N-[3-(Trimethoxysilyl)-propyl]aniline
BINOL	S-(-)-1,1'-Bi(2-naphthol)
BJH	Barrett-Joyner-Halenda
BPC	(S)-(1,1'-Binaphthalene-2,2'-dioxy)chlorophosphine
CNTs	Multi-Walled Carbon Nanotubes
EA	Element Analysis
<i>ee</i>	Enantio-Excess
FTIR	Fourier Transform Infrared Spectroscopy
L/M ratio	Ligand/Metal ratio
MPL	Monodentate Phosphorous Ligands
NEt ₃	Triethylamine
PCl ₃	Phosphorous Trichloride
UV-vis-NIR	UV-visible-Near Infrared
XRD	X-Rays Diffraction

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Chapter 8 Conclusions and Future Perspectives

8.1 Conclusions

In this study, selective hydrogenations of cinnamaldehyde (CALD) and asymmetric hydrogenation of dimethyl itaconate were investigated over supported metallic nanoparticle and metal complex catalysts, respectively. The primary results and findings from these catalytic hydrogenation studies are summarized in this chapter.

Platinum-based mono- and bi-metallic catalysts were synthesized by employing a facile and rapid microwave-assisted polyol reduction (MAPR) method. These catalysts were successfully applied to the selective hydrogenation of CALD to cinnamal alcohol. The hydrogenation performances remarkably depended on the chemical environment of active sites, properties of multi-walled carbon nanotube (CNTs) support surfaces, solvents and promoters. Removal of oxygen-containing groups from CNTs surfaces improved both activity and selectivity, due to the suppressed side reactions and enhanced electron transfer from CNTs to Pt nanoparticles. By screening solvents with different polarities, ethyl acetate (EA) was identified as the best candidate in this reaction and the enhanced activity is hypothesized to be contributed by the presence of parallel transfer hydrogenation steps. The catalytic properties can be promoted by Fe and Co. Compared to impregnation method; MAPR not only served as a facile and time-saving synthesis methodology, but also attained the CNTs-CALD affinity due to the π - π interaction and assisted the metal-metal electron transfer due to the close contact between promoters and Pt nanoparticles. These synergic effects contributed to the significantly improved activity and selectivity.

In order to investigate the role played by synthesized chiral supports in asymmetric hydrogenation, a series of chiral mesoporous silica (CMS) materials with different pore sizes and structures were synthesized by adopting a conventional achiral surfactant as the template along with a chiral cobalt complex (CCC) as the co-template. The CMS channels exhibited local chiral characteristics which can be explained by the existence of the chirally distorted SiO_4 tetrahedrons and $\text{Si}(\text{OSi})_4$ formed during the synthesis. Pt nanoparticles were loaded on the CMS materials and applied in asymmetric hydrogenation of dimethyl itaconate. In spite of the extremely low enantio-excess in this particular reaction, the chiral induction capability of the catalyst should be contributed by the CMS support. The chirality of template-free CMS was further substantiated by enantio-selectively controlled release of a representative chiral drug (metoprolol). The different kinetic release profiles of R- and S-metoprolol from CMS materials can be attributed to the specific interactions between enantiomers and local chiral bonding sites of CMS matrix.

Subsequently, the formation mechanism of CMS materials was studied by using vibrational circular dichroism (VCD) spectroscopy. The pore wall surfaces of CMS materials exhibited local chiral characteristics which can be explained by the existence of asymmetrically distorted SiO_4 tetrahedrons. It was proposed that the rigid CCC with planar chirality incorporated into the sub-layer of micelle and induced the distortion of adjacent surfactants to afford the formation of a chiral aggregation which subsequently transferred the chirality to the silica motif of CMS via electrostatic interactions. Increasing the concentration of CCC resulted in the meso-phase transformation from hexagonal to lamellar which impaired the chirality transfer. This

study contributed to the synthesis of mesoporous silica materials with chiral entities at a molecular level and understanding of the chirality transfer steps from organic template with inherent chirality to inorganic building blocks.

Regarding the weak chiral capability of CMS support in asymmetric hydrogenation, anchoring well-defined homogeneous chiral catalysts on solid support surfaces was attempted in this study. A monodentate phosphoramidite ligand (BPEAn) was synthesized and immobilized on SBA-15 and CNTs surfaces via covalent bond and π - π interaction, respectively. Prior to the immobilization, 80.5% *ee* at 100% conversion was obtained over BPEAn-Rh complexes in the homogeneous asymmetric hydrogenation of dimethyl itaconate, which are comparable to the reported results. Changing the ligand/metal ratio from 2 to 1 did not lead to variations of both conversion and selectivity, implying that monodentate ligand was also active in catalyzing the asymmetric reaction. However, substantially low activity and enantioselectivity were found on immobilized mono-complex on SBA-15 surfaces, which can be attributed to the mass transfer resistance in mesopores of SBA-15 after tethering bulky functional groups and the changes in the nature of immobilized ligand as a result of covalent bonding. Interestingly, an opposite enantio-selectivity was observed when SBA-15 supported homo-complex was employed as catalyst. The unusual phenomenon was tentatively ascribed to the product adsorption in the vicinity of catalytic active centers. Recycle and reuse of the homo-complex covalently bonded on SBA-15 did not show significant loss of activity and enantioselectivity. Remarkably improved catalytic results were obtained over CNTs supported BPEAn-Rh complexes

prepared by adsorption method. Nonetheless, the interaction between active sites and CNTs surfaces was not strong enough to prevent the leaching during the reaction.

8.2 *Future perspectives*

Based on the results recorded in this PhD work, we tentatively proposed several research topics which may be carried out in future. It has been proved that MAPR is a very facile and efficient method to prepared supported Pt nanopartilces. Parameters of this microwave-assisted reduction process, such as time, temperature and heating speed, may affect the size distribution and crystallization of Pt particles. Details of MAPR process and their influence on catalytic performances will be thoroughly investigated.

Based on the results of Chapter 4, catalysts prepared by using impregnation (IMP) method (such as PtFe/CNT-973-IMP) have higher electrochemical active surface (EAS) area than those prepared by MAPR method, but the activities of these impregnated catalysts are low as a result of lack of close contact between promoter and active center. However, IMP is also a very feasible approach to prepare large quantity of catalysts. Therefore, it is worthwhile to improve the conventional IMP method by enhancing the interaction between promoter and active center.

It has been demonstrated that electrochemical measurement is a very efficient way to estimate the number of active centers. However, the measurement is usually conducted in water solution, and for low loading of Pt, the number of active sites is calculated based on the number of adsorbed carbon monoxide, due to the weak signal of hydrogen desorption. While, hydrogenation reactions are performed in organic solvent under high pressure of hydrogen. Thus, the accuracy of this method should be

evaluated by comparing with other techniques, such as hydrogen temperature-programed desorption and calculation based on particle size distribution (which can be obtained by TEM).

Recently, it has been found in a model catalyst that the presence of iron oxide island on Pt surface was highly active for oxidization reactions, e.g., CO oxidization. The configured active sites should also exist on the Pt-Fe bimetallic catalysts prepared by MAPR method, regarding to the close contact between Fe promoters and primary Pt active sites. Thus, these bimetallic catalysts can be applied to the oxidization of benzyl alcohol. Other than removal of the oxygen-containing groups from CNTs surfaces, these functional groups may react with modifiers, e.g., silanes to bond new organic moieties on CNTs surfaces. It will be interesting to study the influence of various organic groups on the electron density of Pt nanoparticles, subsequently the catalytic performances.

Driven by the rapid consumption of available resources and environmental issues, research efforts have been devoted to shift from petro-chemistry to green chemistry. Biomass such as cellulose may partially replace the fossil fuel and become one of the most important feed stocks. Transformation of cellulose to value-added commodity chemicals, such as sorbitol, ethylene glycol and 5-hydroxymethylfurfural can be achieved by hydrolysis and hydrogenolysis of its polysaccharide chain. It has been disclosed that the rate-determining step is hydrogenolysis of the C-O bond in the glucose ring. Since the metal oxide islands on Pt surfaces can efficiently activate the C=O bond during hydrogenation, the similar promoting effect may also play a role in the hydrogenolysis of cellulose.

Fabricating a chiral support surfaces is still of interest, considering its potential applications in both asymmetric catalysis and chiral resolution. This conceptual idea can be extended to other porous materials, e.g., metal-organic framework (MOF). To create a strong chiral environment in MOF, directly using chiral molecules as the building units of chiral MOF materials can be attempted. MPL-Rh complex can be immobilized on CMS materials to further verify the effect of chiral support on asymmetric catalysis. Regarding the rigid and bulky structure of BINOL, modified BINOL molecules may be employed as the spacers of MOF which can also be applied to asymmetric reactions.

List of abbreviations

BINOL	S-(-)-1,1'-Bi(2-naphthol)
CALD	Cinnamaldehyde
CCC	Chiral Cobalt Complex
CMS	Chiral Mesoporous Silica
CNTs	Multi-Walled Carbon Nanotubes
EA	Ethyl Acetate
EAS	Electrochemical Active Surface
IMP	Impregnation
MAPR	Microwave-Assisted Polyol Reduction
MOF	Metal-Organic Framework
TEM	Transmission Electron Microscopy
VCD	Vibrational Circular Dichroism

Appendix

Journal publications

- Zhen Guo, Yuanting Chen, Lusi Li, Xiaoming Wang, Gary L. Haller, Yanhui Yang, Carbon nanotube supported Pt-based bimetallic catalysts prepared by a microwave-assisted polyol reduction method and their catalytic applications in the selective hydrogenation, *Journal of Catalysis*, 2010, 276, 314–326
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- Xianbin Liu, Yu Du, Zhen Guo, Saranya Gunasekaran, Chi-Bun Ching, Yuan Chen, Susanna Su Jan Leong, and Yanhui Yang, Monodispersed MCM-41 large particles by modified pseudomorphic transformation: diamine functionalization and application in protein bioseparation, *Microporous and Mesoporous Materials*, 2009, 122, 114-120
- Yuanting Chen, Wan Chen, Qinghu Tang, Zhen Guo, Yanhui Yang, Fabing Su, Aerobic oxidation of benzyl alcohol over activated carbon supported manganese and vanadium catalysts: effect of surface oxygen-containing groups, *Catalysis Letters*, (in press)

Conference presentations

- Model-aided design of three metals catalyst for selective hydrogenation of cinnamaldehyde, 15th National Congress on Catalysis of China(15 NCC), Nov. 2010, Guangzhou, PRC
- Immobilization of phosphoramidite ligands-Rh complexes on SBA-15 and its catalytic application in conjugate addition of arylboronic acids to enones, 16th Regional Symposium on Chemical Engineering, Dec. 2009, Manila, Philippines
- Synthesis and application of chiral mesoporous silica, 5th Pacific Basin Conference on adsorption science and technology (PBAST5), May 2009, Singapore
- Monodispersed MCM-41 large particles by modified pseudomorphic transformation: diamine functionalization and application in bioseparation of proteins, 5th Pacific Basin Conference on adsorption science and technology (PBAST5), May 2009, Singapore
- Unusual photoelectronic effect from molecular solid material $[\text{Co}(\text{en})_3](\text{Zr}_2\text{F}_{11}\text{H}_2\text{O})$ with mesostructured open-framework, 15th Regional Symposium on Chemical Engineering, Dec. 2008, Kuala Lumpur, Malaysia