Aerobic oxidation of aromatic alcohols over confined noble metal nanoparticles

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**AEROBIC OXIDATION OF AROMATIC ALCOHOLS
OVER CONFINED NOBLE METAL NANOPARTICLES**

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**SCHOOL OF CHEMICAL AND BIOMEDICAL
ENGINEERING**

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Abstract

The selective oxidation of alcohols to the corresponding aldehydes or ketones has involved many efforts from industrial research owing to the irreplaceable importance of these carbonyl compounds in the pharmaceuticals, agrochemicals, and perfumery industries. Concerning the atom economy and environmental demand, heterogeneous catalyst is preferred as a greener alternative to the conventional stoichiometric procedures. Choosing an appropriate support with well-defined structure and suitable surface chemistry is a feasible and effective approach to obtain metal nanoparticles with specific size, shape, structure, and to avoid agglomeration that leading to catalytic deactivation. In this PhD work, the selective oxidation of aromatic alcohols to aldehydes and ketones, particularly benzyl alcohol to benzaldehyde, was tackled as model reaction with the intention of successfully synthesizing more efficient heterogeneous catalysts. Our primary objective is to elucidate the effect of metal nanoparticle confinement on the catalytic activity over supported noble metal catalysts with particular highlights on the interactions between both metal-metal and metal-support.

Highly dispersed noble metal nanoparticles with substantially similar mean particle size were effectively confined in the mesopores of SBA-16 with the unique “super-cage” structure. To study the chemistry of metal-support interactions, the surface of SBA-16 silicas was decorated with different functional groups, which led to great impact on the catalytic performance. Amine-functionalization remarkably improved the selectivity towards benzaldehyde. Au-Pd bimetallic catalysts showed enhanced catalytic performance due to the synergetic effect of Au and Pd, while the size-dependent effect was eliminated. The bimetallic nanoparticles were uniformly alloyed with Pd cluster-on-Au cluster structure.

Nonetheless, considering the limited enhancement of catalytic performance of Au-Pd/SBA16 catalysts due to the mass-transfer restriction in the mesopores of SBA-16, TUD-1 mesoporous silicas were further employed as support. Pd catalysts supported on TUD-1 functionalized with several organic functional groups, especially amino groups, was evaluated for the aerobic oxidation of benzyl alcohol without any inorganic base. TUD-1 outperformed other mesoporous silicas due to its unique open 3-D sponge-like mesostructure which can effectively confine Pd nanoparticles and suppress the mass-diffusion resistance. The type and content of grafted functional groups greatly affected the catalytic performance by tuning the surface basicity, metal particle size and size distribution, and metal-support interaction.

The particle size, morphology, structure and electron properties of metal nanoparticles may be varied by different preparation procedures. Successfully prepared via Ar glow discharge plasma reduction, Au-Pd bimetallic nanoparticles was highly active in the selective benzyl alcohol oxidation, giving a rate constant of 0.50 h^{-1} , which was 12.5-fold of Au catalyst and 2-fold of Pd catalyst, respectively. Characterization analysis attributed this enhancement to a Pd-rich shell/Au-rich core structure with abundant surface coordination-unsaturated Pd atoms of those effectively confined and well dispersed Au-Pd nanoparticles. As a green, efficient and safe protocol, plasma reduction outperformed the conventional H_2 thermal reduction due to a different particle nucleation and growth mechanism which afforded modified morphology and surface chemistry of metal nanoparticles. Further oxidation and re-reduction of plasma reduced Au-Pd catalyst resulted in the atomic re-arrangement of nanoparticles, leading to an inferior catalytic performance with decreased rate constant.

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Chapter 1 Background and Philosophy

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

The carbonyl compounds, including aldehydes and ketones, are produced mostly from the selective oxidation of alcohols at the presence of the catalyst and oxidant, as shown in Scheme 1.1. The R and R' substitution groups can be alkyl, aryl and hydrogen. It has an annual production world-wide of over 107 tons and is essential as intermediates in organic transformation as well as being high value components for the pharmaceuticals, agrochemicals, and perfumery industry. In particular, benzaldehyde is an important component to produce a variety of other aldehydes, such as cinnamic, methylcinnamic, amylcinnamic, and hexylcinnamic aldehydes.

Scheme 1.1 The selective oxidation of alcohols to aldehydes or ketones.

In the selective oxidation of alcohols, the conventionally applied stoichiometric oxygen donors, such as chromate, permanganate or bromate, are not preferred due to their high cost, toxicity and formation of a large amount of wastes. From both the economic and environmental point of views, using molecular oxygen/air as a green oxidant with water as the only byproduct has been a much more promising catalytic protocol with low expense. In spite of the introduction of molecular oxygen/air as a clean oxidant, most studies carried the catalytic reaction in the presence of organic solvent such as toluene and benzene, which is not

environmentally friendly. Therefore, solvent-free conditions are more preferred in the present study.

Transition metals such as Co (II), Cu (II) or Ni (II) in the form of metal salts or organic complexes, effectively catalyze the selective oxidation of alcohols as homogeneous systems at both laboratory and industrial scale [1]. From the standpoints of atom economy and environmental demand, more and more attention has been paid to the development of heterogeneous catalysts using transition metals as a green alternative [2-4].

1.2 Motivation and outline of this dissertation

In the selective oxidation of alcohols, the catalytic activity of noble metal based heterogeneous catalysts heavily relies on the interaction between both metal-metal and metal-support. It can be specified as the following three factors: metal cluster size, the synergistic action of metal-metal, and the interaction between the metal and the support.

It has been proved in many studies that the size of the noble metal nanoparticles plays a key role in determining the catalytic activity in the aerobic selective oxidation of alcohols. Active phases, *i.e.*, metal nanoparticles, have different properties such as crystallographic facets, fraction of surface atoms and electron properties with different size, which therefore exhibits different catalytic activity and makes it interesting to study the size effect on catalytic activity. For example, it has been reported that in CO oxidation, the activity of the supported Au clusters is significantly enhanced when the diameters of Au nanoparticles are below 5 nm [2], as shown in Figure 1.1. However, in the glucose oxidation, the active phase Au nanoparticles does not easily donate electrons to the adsorbed molecular oxygen as the role in CO oxidation but is polydispersed and has

complex interaction with the support and the catalytic activity starts to increase when the size decreases below 10 nm and independent to the surface area in the size range of 3.6-6.5 nm [3]. The synergistic electronic interaction between bimetal atoms in the individual nanoparticles has been demonstrated to play an essential role in the enhancement of improving the catalytic properties for the selective oxidation of alcohols compared to the monometallic system [4]. The formation of bimetallic nanoparticles by adding one component to another is suggested to not only improve the catalytic activity and selectivity but also enhance the resistance to the deactivation [5].

Figure 1.1 Size-dependent effect in CO oxidation [2].

It has been found that metal exhibits excellent catalytic activity in the nanocrystalline form as a collection of a few hundreds of atoms. However, metal nanoparticles have a tendency to aggregate which will dramatically decrease the number of available active sites. A feasible and effective approach to avoid agglomeration is to disperse the metal nanoparticles on an appropriate support through a specific interaction with support or a well-designed steric confinement imposed by the support. Many supports have been employed to synthesize

heterogeneous catalysts for the selective oxidation of alcohols, such as polymers [6-8], metal and non-metal oxides [9-12], micro- and mesoporous materials [13-16], *etc.* Since the first preparative method for dispersing of metal nanoparticles in aqueous solution by Faraday [17], supported metal nanoparticles have been produced by chemical reduction of the corresponding metal precursors in solution in the presence of suitable supports. At present, there are several well-established synthesis methods available such as impregnation [18-21], deposition precipitation [12, 18, 22-23], co-precipitation [18], grafting [24-25], *etc.* In most of the heterogeneous catalysts, metal nanoparticles are supported on the external surface of the substrate. With the development of heterogeneous catalysis, the widely use of micro- and mesoporous silicas has become a general strategy to increase the total surface area and have some control on the selectivity of the process. Since the discovery of MCM-41 in 1992 [26], there is an obvious interest in using these porous solids as host to stabilize and confine the active phases. These novel supports have novel properties that unlike those of conventional metal oxides such as TiO_2 and Al_2O_3 : highly ordered mesopores, controlled pore size, specific surface areas of about $1000 \text{ m}^2 \text{ g}^{-1}$, and pore volumes of about 1 mL g^{-1} . These materials have been the promising and preferred hosts to incorporate the active phases within the internal void space to exhibit fantasy catalytic properties. However, the affinity between these metal nanoparticles formed by hydrogen reduction from metal precursors and the support surface is so low that these nanoparticles can be easily removed by solvent extraction. In addition, the surface chemistry of the support is also playing an important role in catalytic behaviors. The arise of functionalization the support surface with the appropriate functional

groups can avoid this problem and strongly retain the active phases inside the micro-/meso- pores of the substrate.

However, it is hard to clearly figure out the effect of each factor in the process since these factors can affect simultaneously, resulting in an ambiguous explanation. Based on the high desire to investigate the effects of each factor on the catalytic performance, the common “tail-and-error” method is introduced, in which each factor will be adjusted while keeping others constant. Considering that the size effect has been extensively studied, in our study, we put our emphasis on the support effect and the synergistic effect and try to exclude the size effect by controlling the particles in a specific size range. Some supports have highly ordered nanopores/nanochannels of several nanometers and can confine the metal nanoparticles within the nanostructure while still being catalytic active to the selective oxidation of alcohols, such as SBA-16 with 3-D cubic cage-like structure, TUD-1 with 3-D sponge-like structure, and SBA-15 with 2-D hexagonal structure. Therefore, choosing an appropriate support with particular nano structure and functionalized surface to make metal nanoparticles with desired size, shape, and structure has been a feasible and effective approach to elucidate the support effect and the synergistic effect on the catalytic performance. In this PhD study, novel nano-structured supports, *e.g.*, SBA-16, TUD-1 and SBA-15, will be applied to confine Au, Pd monometallic and Au-Pd bimetallic nanoparticles in the nano channels, leading to a uniform particle distribution in a specific size range. The support effect (including surface chemistry) and the synergistic effect between bimetal will be carefully studied and elucidated.

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Chapter 2 Literature Review

2.1 Benzyl alcohol oxidation

Benzaldehyde, one of the most essential raw materials in chemical industry, has been widely employed as an intermediate in synthetic dyes, flavor and pharmaceuticals. Moreover, it is also an important component utilized to produce a variety of other aldehydes, such as cinnamic, methylcinnamic, amylcinnamic, and hexylcinnamic aldehydes. Catalytic technologies leading to high quality grade benzaldehyde has attracted extensive attention. Benzaldehyde was originally synthesized by the alkali hydrolysis of benzal chloride derived from toluene chlorination [1]. In recent years, several industrial processes of benzaldehyde production have been developed, including toluene gas/liquid phase oxidation [2-3], benzyl alcohol oxidation [4], benzoic acid reduction [5], toluene indirect electro oxidation [6], toluene manganese sesquioxide heterogeneous oxidation [7], toluene bionic catalytic oxidation [8], toluene oxidation in super (sub) critical fluids [9], and cinnamaldehyde hydrolysis in subcritical water [10]. However, some of these technologies involve the benzoic acid and/or organic chlorine contamination. Some processes require the high operation cost due to the severe reaction conditions such as high temperature and pressure. Some processes cannot satisfy the high demand on benzaldehyde production due to the poor conversion and selectivity with large amount of byproducts. Moreover, in the gas phase oxidation, the total oxidation of benzyl alcohol to carbon oxides is impossible to avoid, resulting in a significant decline of carbon efficiency.

Compare to the above-mentioned processes, the liquid-phase selective oxidation of benzyl alcohol to benzaldehyde using air or molecular oxygen under mild solvent-free reaction conditions is much more preferable from the viewpoints

of environmental benign and atom economy concerns. This process has been considered as one of the most important organic transformation reactions due to the environmentally friendly production of chlorine-free benzaldehyde, the high reaction selectivity which avoid the non-desired and costly byproducts, and the elimination of the greenhouse gas CO₂ emission.

Benzyl alcohol oxidation is also frequently employed as a model alcohol oxidation in the laboratory study due to its relatively high reactivity. The main product benzaldehyde is a non-enolizable aldehyde, which reduces the number of possible side products. The possible reaction network of benzyl alcohol oxidation is shown in Scheme 2.1. Enache et al. suggested that benzyl benzoate is derived from aldol condensation between the generated benzaldehyde and the initial benzyl alcohol [11]. Li et al. proposed that benzaldehyde may also come from the disproportionation of benzyl alcohol other than the direct oxidation [12]. However, most researchers [13-14] suggested, which is also generally accepted, that benzyl alcohol is firstly oxidized to benzaldehyde, further oxidized into benzoic acid, and benzyl benzoate is produced from the esterification between benzyl alcohol and benzaldehyde. Moreover, the disproportionation of benzyl alcohol cannot be ignored as well, as shown in Scheme 2.1. The selective oxidation of benzyl alcohol to benzaldehyde is a typical dehydrogenation reaction and the reaction mechanism is shown in Scheme 2.2. The first step is the oxidation of benzyl alcohol by dehydrogenation, which results in the formation of benzaldehyde and adsorbed hydrogen on the metal surface. In the second step, the adsorbed hydrogen is removed from the metal surface by oxidation with oxygen and produce water as the byproduct.

Scheme 2.1 The process of benzyl alcohol oxidation.

Scheme 2.2 The reaction mechanism of the selective oxidation of benzyl alcohol.

2.2 Metal catalysts

Many homogeneous catalysts, in the form of either metal salts or organic complexes, have been developed to effectively catalyze the aerobic selective oxidation of benzyl alcohol at both laboratory and industrial scale [2-4]. Homogeneous catalyst possesses several advantages, including good catalytic activity and high selectivity towards desired benzaldehyde products. However, homogeneous catalysis process, which usually requires expensive additives such as sodium acetate, sodium hydroxide and potassium carbonate, has some intrinsic drawbacks such as the high operation cost and the generation of aqueous effluents

containing large amounts of inorganic salts [15-16]. Therefore, from the standpoints of atom economy and environmental demand, rapid growing attention has been paid to the development of heterogeneous catalysts as a “greener” alternative to replace the conventional stoichiometric procedures. Several apparent advantages, such as high resistance to leaching, simple product isolation, good recyclability, and readily availability from catalyst manufactures in various forms and compositions, make heterogeneous catalysts extremely attractive in designing an environmentally clean process [17]. It has been evidently demonstrated in numerous literatures that such heterogeneous oxidations undergo an oxidative dehydrogenation mechanism, *i.e.*, the substrates are first adsorbed and dehydrogenated on the activated metal surfaces, followed by the oxidation of the adsorbed hydrogen atoms by the corresponding oxidizing agents [18-20].

The examples of heterogeneous catalyzed alcohol oxidations using inexpensive transition metals, such as Ni [21], Cu [22], V [23] and Mn [24-26] has been reported. In spite of the inspiring progress in successfully modifying the supports with less expensive transition metals in aerobic oxidation of alcohols [27-28], some persistent problems still exist. First, organic solvents are generally applied, which the resulting mixtures of the organic substrates, products, and solvents are difficult to separate. Second, severe reaction conditions have to be introduced to successfully perform the oxidations, such as high temperature and high oxygen pressure. Finally, the catalysts only show activity for specific types of alcohols, which limits the application of such catalysts. The use of supported or confined monomeric and nano-sized noble metals for the aerobic oxidation of benzyl alcohol has risen as a new trend and been widely investigated in the last decades [29-31]. Among various noble metals, gold and palladium catalysts have attracted considerable attention due to their superior

catalytic performance. Numerous literatures have been reported on the investigation on Au and Pd heterogeneous catalysts in the selective oxidation of benzyl alcohol [27, 32-41].

Gold chemistry, both in homogeneous and heterogeneous catalysis, has not risen up as one of the new promising research area until the last few decades. Historically, gold was largely considered as a noble and inert metal, it did not exhibit any catalytic activity for redox reactions [42-43]. The traditionally views over inert gold was completely overthrown after Hutchings predicted that gold would be the most active catalyst for the selective hydrochlorination of acetylene in 1985 [44]. The first discovery that gold nanoparticles showed extremely high activity for low-temperature CO oxidation was reported by Hartua et al. in 1987 [45]. Thereafter, tremendous efforts have been made to develop various types of gold-based catalysts in the form of supported nanoparticles of metal complex, exhibiting interesting and promising catalytic activity in many fields, such as the direct synthesis of hydrogen peroxide [46], hydrochlorination of alkynes [44], and oxidation of alcohols and aldehydes [11, 47]. Prati and Rossi were the first to clearly proved that carbon supported Au catalyst can be effective for the liquid phase oxidation of alcohols, including monohydroxy alcohol, diols, and polyols such as sugars, as long as the presence of base [48-49]. Abad et al. have shown that cerium oxide supported Au catalysts is exceptionally active for the oxidation of 1-phenylethanol under mild solvent-free conditions, giving an extraordinary high turnover frequency (TOF) of $12\ 500\ \text{h}^{-1}$, which is the benchmark in heterogeneous catalysts for the aerobic oxidation of alcohols [33].

Literatures [50-53] have reported the study on palladium catalysts since the first successful application of Pd in catalyzing aerobic oxidation of alcohols was

discovered in 1977 by Blackburn and Schwartz [28]. More and more effort has been paid to develop the heterogeneous Pd catalysts with outstanding catalytic activity as well as good stability [54]. For instance, Pd on TiO₂ [55], Pd on activated carbon [56], Pd on pumice [57], Pd-hydrotalcite [58], and Pd on polymers [59]. Uozumi and Nakao reported that polystyrene-poly(ethylene glycol) resin supported palladium nanoparticles with the mean particle size of ca. 9 nm exhibited high efficiency and selectivity in the aerobic oxidation of a variety of alcohols, and benzyl alcohol can be almost completely converted to benzaldehyde in 90 min using molecular oxygen over Pd dispersed on an amphiphilic resin (Pd-ARP) [60]. Mori et al. have shown that hydroxyapatite supported Pd (Pd/HAP) catalysts are highly effective for the oxidation of 1-phenylethanol under mild solvent-free conditions, giving a high TOF of 9 800 h⁻¹ [32]. More recently, Li et al. have reported that zeolite-supported Pd nanoparticles with a mean diameter of 2.8 nm possessed an unusual efficiency (TOF of 18 800 h⁻¹) for solvent-free 1-phenylethanol aerobic oxidation [61].

From both the scientific and technological point of views, bimetallic nanoparticles composed of two different metal elements are of greater interest than monometallic ones for improving the catalytic properties due to the synergetic effect [62]. It has been demonstrated that adding Au to Pd and Pt catalysts not only improves the catalytic activity and selectivity, but also enhances the resistance to the deactivation [63-64]. Hutchings and co-workers have reported that supported Au-Pd alloys, in particular Au-Pd/TiO₂, showed highly efficient catalytic activity for the direct synthesis of H₂O₂ at low temperature [46, 65]. Recently, several groups have examined the supported Au-Pd bimetallic catalysts with remarkably elevated catalytic activity and product selectivity of alcohol oxidation reactions. Enache et al. demonstrated that among a series of Au-Pd alloy catalysts over various supports,

Au-Pd/TiO₂ presented the best selectivity and highest TOF (269 000 h⁻¹) for 1-phenylethanol selective oxidation, showing that the combination of gold and palladium in an alloy nanoparticle configuration leads to a twenty five-fold improvement in catalytic activity [63].

The outstanding advantage of bimetallic catalysts is attributed not only to the electronic interaction between two alloyed metals but also to the complex structure of the bimetallic nanoparticles [66]. Several studies have tested the structures of bimetallic nanoparticles, such as a core-shell structure [63, 67-73], a cluster-in-cluster structure [74], and a single alloy structure [62]. Seven generally accepted morphologies of bimetallic nanoparticles are built and summarized, as depicted in Figure 2.1. He et al. [75] suggested that these different morphologies can be classified according to the continuity of a metal phase. The particle-in-particle structure is made of a continuous outer particle and inner discontinuous particles. In the case of particle-on-particle structure, the outer particles are discontinuous while the inner particle constitutes a continuous particle. Both of the two metal phases are discontinuous in the aggregated structure while continuous in the core-shell bimetallic particle. Nevertheless, it is obvious that homogeneous alloy structure forms a new phase which is different from either of the two metals. More recently, Lee et al. have also reported the three-dimensional flower-shaped porous Au-Pd alloy nanoparticles with a Pd-enriched surface [76].

Figure 2.1 Schematic illustrations of seven possible morphologies of bimetallic nanoparticles.

2.3 Supports

It has been indicated in many studies that the support-catalyst interaction is a crucial factor controlling catalytic activity. Different supports will result in different catalytic performance even loading the same metal catalyst. The primary role of support is to reduce the mobility of the metal nanoparticles to diminish their tendency of agglomeration. In addition, it has also been addressed in some cases that the metal-support perimeter interface acts as a site for activating at least one of the reactants [77]. Up to date, a number of different supports have been tested in the alcohol oxidation, such as polymers [78-80], metals and metal oxides [26, 77, 81-82], micro- and mesoporous materials [61, 83-85], *etc.*

Polymers are introduced as stabilizers for metal nanoparticles due to both the steric bulk of their framework and the weak binding to the metal nanoparticle surface through heteroatom as ligands. Polymers stabilized Au, Pt, Pd catalysts have shown high efficiency in the benzyl alcohol oxidation [86].

Poly(*N*-vinyl-2-pyrrolidone) (PVP) is the most generally used polymer for metal nanoparticle stabilization and catalysis because it can fulfill both steric and ligand requirements [27]. Core-shell bimetallic Au-Pd catalysts supported on PVP have been nicely developed [64, 75]. It was proposed that the PVP can effectively prevent the agglomeration of metal nanoparticles during the catalytic oxidations [87].

Numerous literatures have reported on the catalytic properties of metal nanoparticles supported on oxides, either metal oxides or non-metal oxides. Metal nanoparticles supported on high surface area oxides shows many interesting types of catalytic behaviors. They cover a size range intermediate between the atomic/molecular regime on the one hand and the bulk on the other hand. For about a decade through the 1980's there was a great deal of attention paid to what was then called "strong metal-support interactions" or SMSI and the effect that this chemistry had on catalytic reactions. Many metal oxides have been applied as supports in the benzyl alcohol oxidation, such as Al_2O_3 [26], ZrO_2 [23, 82], CeO_2 [4, 88], *etc*, due to their good stability at high temperature. The most widely employed metal oxide support is TiO_2 . TiO_2 -supported catalysts were found to be most selective and were examined in great detail for the oxidation of benzyl alcohol at 373 K with molecular oxygen as oxidant in the absence of solvent [63]. Recently, a new family of materials similar to TiO_2 has been reported, including nanotubes and nanowires of alkali metal titanates prepared simply by hydrothermal treatments of TiO_2 in the presence of an alkali metal base [89-90].

Among various non-metal oxides, silica is attractive due to its mild acidity, relative inertness and good mechanical properties. Since the discovery of MCM-41 in 1992 by the researchers at Mobil oil Corporation [91], the mesoporous silica, such as MCM-41 [92], MCM-48 [93-94], SBA-15 [85], SBA-16 [84] and TUD-1 [83]

have been intensively studied and demonstrated to be good supports due to their high thermal and hydrothermal stability, large surface area ($\sim 1000 \text{ m}^2 \text{ g}^{-1}$) and uniform pore size (2.0-10.0 nm). Mesoporous silica possess ample silanol groups (-SiOH) which provide the possibility of immobilizing catalytically active phases on the surface of mesoporous silicas. Moreover, the uniform mesopores, such as the 2-D hexagonal structures of MCM-41 and SBA-15 with different pore size, the 3-D bicontinuous cubic structure of MCM-48, the 3-D cubic cage-like structure of SBA-16 and the 3-D sponge-like structure of TUD-1, can effectively confine the metal nanoparticles as superior heterogeneous catalysts. Lee et al. demonstrated that the pore structure and pore size of mesoporous silica hosts play a key role in determining the size and thermal stability of the supported metal nanoparticles, such as big and irregular Au particles situate on MCM-48 whereas homogeneous and small Au particles maintain inside SBA-15 [94].

Among these mesoporous silica materials, SBA-16 first evoked our great attention due to its highly interconnected 3-D cage-liked mesostructure corresponding to the *Im3m* space group [95-100]. It has been reported by Glomm et al. that different functionalization strategies have different effects on both the pore structure of the SBA-16 and the incorporation of gold nanoparticles into SBA-16 [93]. Our group reported a modified method to synthesize SBA-16 mesostructured silica under refluxing condition using block co-polymer poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) (F127) as template, cetyltrimethylammonium bromide (CTAB) as co-template, and tetraethyl orthosilicate (TEOS) as silica source. The resulting SBA-16 silica exhibited highly ordered mesoporous structure, mono-dispersed spherical morphology, and excellent hydrothermal, thermal and mechanical stabilities. It was worth mentioning that the

synthesis time can be significantly reduced from 48 h to 8 h, which opened a feasible way to produce SBA-16 silica in a large scale. Moreover, the “super-cage” pore structure of SBA-16 provides great possibility to encapsulate metal nanoparticles in a “ship-in-a-bottle” way, resulting in highly activity in selective benzyl alcohol oxidation [84].

A recent addition to the mesoporous material family is the so-called TUD-1 mesoporous silica [101]. In the synthesis of TUD-1, surfactant and/or block co-polymer are replaced by inexpensive triethanolamine molecules as the structure directing agent. Interestingly, the unique open 3-D sponge-like wide mesoporous structure of TUD-1 can effectively decrease the pore diffusion resistance as previously demonstrated [83].

It has been extensively demonstrated that the key point in the synthesis of an active metal catalyst is to successfully form the well-dispersed metal particles within the nanometer size range. Choosing an appropriate support with particular structure such as mesoporous silica materials and carbon materials has been a feasible and effective approach to make metal nanoparticle with specific size, shape and structure and avoid aggregation leading to deactivation. Some unique structures of support can protect the active phase from reactant poisoning [102]. Furthermore, it was also found that the catalytic activity of noble metal nanoparticles is tightly associated to the surface chemistry of the support [85, 103-105]. Romanmartinez et al. carefully investigated the influence of support surface chemistry and metal precursor species on the properties of Pt/C catalysts [106]. The obtained results revealed that the distribution of the platinum precursor on the carbonaceous supports and the metal precursor-support interaction are strongly dependent on the support surface chemistry, *i.e.*, on the amount and the nature of the surface oxygen complexes.

Various methods, such as aerosol-assisted self-assemble, the sonochemical reduction of metal salts, and the surface-functionalization using specific functional groups, have been employed to confine the metal nanoparticles within the mesoporous channels of MCM-41, MCM-48, SBA-15 or at the surface of other supports [14, 105, 107-114]. However, the metal nanoparticles can be easily removed by solvent extraction due to the low affinity between these metal nanoparticles formed by hydrogen reduction of metal salts and the support surface. The presence of silane modifiers can functionalize the support surface with the appropriate organic group before the adsorption of metal precursor. These organic functional groups, such as mercaptopropyl, propylamine and polydentate amine ligands, act as anchors to facilitate the immobilization of metal nanoparticles, thereby avoiding the addition of external capping agents such as alkylamines or alkylthiols [115-116]. In addition, it was also demonstrated that these organic functional groups can act as active centers in multifunctional catalysts due to their acid-base or red-ox properties [117]. Ghosh et al. proposed that metal nanoparticles confined in the surface-functionalized support can be taken as a three-layered composite, where the outer sphere is the support, the second sphere is the organic functional groups covalently attached to the support inner surface, and the third sphere consists of the nanoparticles confined in the pore by hooking to the functional groups [92]. Bore et al. have reported that, after amine-functionalization, the tortuous pore arrangements within the spherical mesoporous silica can successfully confine Au nanoparticles, and restrict the mobility of species which leads to thermal sintering and growth of nanoparticles [102]. Aprile et al. have successfully synthesized a mesoporous material mpAu-SiO₂ by one pot procedure using the quaternary ammonium stabilized colloidal gold particles in combination with TEOS

as building blocks [118]. The well dispersed Au nanoparticles, which are embedded inside the mesopores of structured silica, show promising activity and reusability for the aerobic solvent-free oxidation of 1-phenylethanol, giving a high turnover number (TON) of 3000. It has been reported by Takenaka et al. that CNT-supported Pt nanoparticles covered with silica layers using hydrolysis of 3-aminopropyl-triethoxysilane (APS) and/or tetraethoxysilane (TEOS) demonstrate high catalytic activity in methane combustion [119]. Siril demonstrated that co-condensing route leads to higher levels of functionalization than the post-synthesis grafting route and co-condensed propylsulfonic acid functionalized SBA-15 can completely catalyze benzyl alcohol to benzaldehyde after about 2 h [120].

2.4 Oxidizing agent

Conventionally, the selective oxidation of alcohols is usually carried out using stoichiometric oxygen donors, such as chromate [121], permanganate [122] or bromate [123]. However, from both economic and environmental point of views, these stoichiometric oxidizing reagents are not preferred due to their high cost, toxicity and production of a large amount of wastes [121-122], therefore leading to impracticability in the industry production. Growing ecological and economical restrictions lead to an urgent driving force for the development of selective oxidation using the eco-friendly oxidizing agents in the presence of heterogeneous catalysts to replace the polluting processes based on the stoichiometric oxidants. Currently, hydrogen peroxide (H_2O_2), tert-butyl hydroperoxide (TBHP), and molecular oxygen/air are the most prevalent oxidizing agents. However, the use of H_2O_2 and TBHP as oxidants has been found to cause several inherent problems. It has been identified by Arends et al. that the use of H_2O_2 makes the active sites on many

heterogeneous catalysts more susceptible to leaching by solvolysis of the metal-oxygen bonds that anchor them to the surface [124]. For TBHP, it requires long reaction time due to the addition of a corresponding low boiling solvent to favor high yield. Moreover, tert-butanol is left after consumption of TBHP as a co-byproduct, which increases the difficult for product separation. Therefore, using molecular oxygen/air as a green oxidant with water as the only byproduct, has been a much more promising and popular catalytic protocol with low expense (molecular oxygen is much cheaper than other oxidizing reagents). Recently, many highly efficient systems have been developed for catalytic aerobic oxidation of alcohol by molecular oxygen using various metal supported catalysts [25, 32, 63, 125]. Ten Brink et al. reported an extremely effective catalyst of water-soluble palladium (II) bathophenanthroline complex with high conversion and selectivity for the selective oxidation of a wide range of both primary and secondary allylic, benzylic, and aliphatic alcohols using air as the oxidant [53]. A detailed investigation was carried out by Choudhary et al. and it was demonstrated that chlorine-free benzaldehyde can be produced through the solvent-free selective oxidation of benzyl alcohol by molecular oxygen over nano-gold supported on U_3O_8 , particularly prepared by the homogeneous deposition precipitation method [126]. Fristrup et al. studied the gold-catalyzed oxidation of a series of para-substituted benzyl alcohols using molecular oxygen and proposed that the rate-determining step involves the generation of a partial positive charge in the benzylic position, *i.e.*, hydride abstraction [127].

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Chapter 3 Techniques of Characterization, Synthesis, and Catalytic oxidation

In the catalysis research, characterization techniques are essential and indispensable to investigate the physico-chemical properties of catalysts, such as bulk and local structure, morphology, and chemical compositions, which play a vital role in the catalytic behaviors. With the thoughtful characterization results on a molecular/atomic level, the design and modification of catalyst with improved performance can be conducted more rationally and readily. Understanding the fundamental concepts of the characterization techniques is absolutely basic to appropriately take the advantage of them, which will be briefly described in this chapter as well as the synthesis methodologies of the support materials and catalysts in this thesis.

3.1 Characterization techniques

3.1.1 Characterization of catalyst morphologies and structures

X-ray diffraction (XRD), which is based on the elastic scattering of X-rays from the electron clouds of the individual atoms in the system, has been widely employed to identify and characterize the crystallographic structure, crystallite size (grain size), and preferred orientation in polycrystalline (*e.g.*, metal crystallites [1]) or powdered solid samples with ordered structure (*e.g.*, mesoporous materials [2] and zeolites [3]). For mesoporous molecular sieves, XRD signals are derived from the ordered nano-sized pore walls in crystals rather than uniform arrangement of atoms. Both the position (corresponding to lattice spacing) and the relative intensity of the distinctive diffraction pattern are indicative of a particular phase and material, providing a "fingerprint" for comparison. In this thesis, powder XRD measurements were conducted on a Bruker AXS D8 X-ray diffractometer (Cu K α , $\lambda=1.5406 \text{ \AA}$, 40 kV, 30 mA) under ambient conditions. Diffraction data were collected with a

resolution of 0.02° (2θ) for both high angle ($10-80^\circ$) and low angle ($1-8^\circ$) measurements. Prior to test, samples were dried at 373 K overnight. The average crystallite sizes were estimated based on the full width at half maximum of well resolved diffraction peaks using Scherrer's equation with a Scherrer constant of 0.89 [4]. The lattice constants were derived following the Cohen procedures [5]. The phase identification was made by comparison to the Joint Committee on Powder Diffraction Standards (JCPDSs)

Physical adsorption (physisorption) is a primary method and has been extensively used to characterize the texture and structure properties of porous materials. The porosity information such as specific surface area, pore volume, pore size and pore size distribution, can be extracted based on the isotherms of sorption. Mesoporous materials (*e.g.*, MCM-41, MCM-48 and SBA series) typically follow the type IV isotherm, which gives a sharp increase in adsorption volume indicative of the capillary condensation in mesopores [6]. In this report, nitrogen adsorption-desorption isotherms were measured at 77 K using a Quantachrome Autosorb-6b static volumetric instrument. Prior to each measurement, the samples were degassed at 523 K for 6 h to a residual pressure below 10^{-4} Torr. A Baratron pressure transducer (0.001-10 Torr) was used for low-pressure measurements. The specific surface area was calculated using Brunauer-Emmet-Teller (BET) method [7]. The pore size and pore size distribution were calculated by the Barrett-Joyner-Halenda (BJH) method using the desorption branch of isotherms [8].

Transmission electron microscopy (TEM) enables the direct observations on the aggregation state, size, morphology and structures, which are the first concerns of nanosized materials. Metal nanoparticles, especially those consisting of noble metal elements, give high contrast after dispersed on thin carbon films. Owing to a

rapid improvement in high-voltage electron beam technique, high resolution TEM (HRTEM) can now provide information not only on the particle size and shape but also on the crystallography of mono- and bi-metallic nanoparticles, giving the atom arrangement and atomic-scale defects in the specimen. In this thesis, TEM was performed on a JEOL JEM-2010, operated at 200 kV. The samples were suspended in ethanol and dried on holey carbon-coated Cu grids. The mean particle diameter was calculated from the mean frequency distribution by counting ca. 200 particles according to: $d = \frac{\sum n_i \cdot d_i}{\sum n_i}$ where Σ is the sum of i over the entire sample, n_i is the number of particles with particle diameter d_i in a certain range. The corresponding root mean square error σ was determined using the following statistical expression: $\sigma(d) = \sqrt{\frac{\sum n_i (d - d_i)^2}{\sum n_i - 1}}$. As a complement to obtain localized elemental information, Energy-dispersive X-ray spectroscopy (EDX) was carried out using the same microscope with an EDX detector (Oxford Instruments, UK). Scanning Transmission Electron Microscopy-EDX (STEM-EDX) was also conducted using the same equipment combined with a Sirion200 field emission Scanning Electron Microscope.

3.1.2 Characterization of catalyst active sites

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. Hydrofluoric acid was used to dissolve silica-based samples whereas nitric acid was used for metal oxides-based samples.

The pH of surface-functionalized mesoporous silica materials with different organic groups was measured following the method reported by Tian *et al.* [9]. A

concentration of 0.2 mg of dry sample was added to 10 mL of hot fresh distilled water, boiled for 5 min, cooled to room temperature, and stirred overnight to reach equilibrium. The suspension was filtered and the pH of the filtrate was measured by a pH meter.

A molecule would undergo electronic transitions when it absorbs or reflect light in the ultraviolet (UV) and visible (vis) ranges, *i.e.*, the electrons are excited by the absorbed energy into an empty, higher energy orbital. A UV-vis spectrum can be obtained by plotting the absorbance of energy against the wavelength. UV-vis spectroscopy has widespread applications, such as determination of the oxidation state of a metal center [10], detection of eluting components in high performance liquid chromatography (HPLC) [11], or determination of the maximum absorbance of a compound prior to a photochemical reaction [12]. For metal nanoparticles, particularly Au, Ag, and Cu (Group 1B metal) which have characteristic colors related to the particle size, UV-vis spectra can be a useful complement in characterizing the particle dispersions. Furthermore, the formation processes of bimetallic nanoparticles, *i.e.*, the reduction of metal ions and the aggregation process, can also been revealed in situ UV-vis observation. In this thesis, to examine the local environment of metal incorporated into the framework of silica mesoporous materials, diffuse reflectance UV-vis spectroscopy was employed and recorded on a VARIAN 5000 UV-vis-NIR spectrophotometer with a diffuse reflectance accessory. The spectra were recorded in the range of 200-800 nm at room temperature with BaSO₄ as a reference. All samples were dried at 373 K overnight before performing the test.

X-ray photoelectron spectroscopy (XPS) is a powerful tool in the quantitative and qualitative analysis of the surface composition and structures of catalysts, which

are indispensable to elucidate the catalytic properties. In this PhD work, XPS measurements were performed on a VG Escalab 250 spectrometer equipped with an Al anode (Al Ka = 1486.6 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. The correction of the binding energies (BE) used the C1s peak of adventitious C at 284.6 eV. The background contribution caused by inelastic process was obtained by Shirley method and subtracted. The curve fitting was done with a Gaussian–Lorentzian function to deconvolute the overlapped peaks. The atomic ratios of the different elements were estimated using the ratio of the normalized peak intensities corrected with the atomic sensitivity factors (5.240 for Au4f, 4.462 for Pd3d, 0.711 for O1s, and 0.283 for Si2p).

Fourier Transform Infrared (FTIR) Spectroscopy is most useful for identifying types of chemical bonds (organic/inorganic), and quantitatively determining the components or consistency of a mixture. In FTIR measurement, an IR spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas molecular is obtained when IR radiation is passed through, creating a unique molecular fingerprint of the sample. Moreover, the surface chemistry of catalyst can be studied by introduction of adsorbed small molecules, particularly carbon monoxide (CO), which can be easily adsorbed on metals. The wavenumber and adsorption mode of adsorbed CO primarily depend on the metal and surface structure. For bimetallic nanoparticles, the surface micro-structure can also be elucidated. In this thesis, FTIR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer at room temperature ($4000\text{--}450\text{ cm}^{-1}$, resolution of 1 cm^{-1}). The sample was pressed into pellet with KBr and placed into an in situ IR cell with CaF₂ windows. After alignment, the sample compartment was subjected to a thermal

pretreatment under a helium atmosphere at 393 K for 2 h to remove the moisture. The data were collected at room temperature (resolution of 1 cm^{-1}). Diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy of adsorbed CO was obtained on a Tensor 27 spectrometer (Bruker) equipped with a liquid nitrogen cooled mercury-cadmium-tellurium (MCT) detector, a diffuse reflectance accessory and a high temperature reaction chamber (Praying Mantis, Harrick). The powder (7 mg) was loaded into the reflectance cell and purged by flowing helium (20 mL min^{-1}) at 573 K for 1 h to remove gas phase and weakly bound water. CO adsorption was carried out in 1.11 vol.% CO/He (20 mL min^{-1}) for 30 min at 298 K, followed by purging with He (20 mL min^{-1}) for another 30 min at the same temperature. The *in-situ* DRIFT spectra were recorded with 64 scans at 4 cm^{-1} resolution and illustrated using Kubelka-Munk (K-M) units, which is linear with the concentration of surface species.

3.2 Synthesis methodologies

3.2.1 Materials

Hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), palladium chloride (PdCl_2), palladium nitrate dihydrate ($\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$), sodium chloride (NaCl), Hydrochloric acid (37%), Sulfuric acid (H_2SO_4 , 98%), ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25%), n-butanol (BuOH , 99.8%), absolute ethanol (EtOH), acetone (HPLC grade), ethyl acetate (EA), benzyl alcohol (98%), toluene (>99.9%), 1-phenyl ethanol (98%), *p*-methylbenzyl alcohol (99%), *p*-methoxybenzyl alcohol (99%), *p*-nitrobenzyl alcohol (99%), *p*-bromobenzyl alcohol (99%), (3-aminopropyl) triethoxysilane (APS), [3-(2-Aminoethylamino)propyl] trimethoxysilane (ATMS), hexamethyldisilazane (HMDS), (3-Mercaptopropyl) trimethoxysilane (MPTMS), hexadecyltrimethylammonium bromide (CTAB), were purchased from

Sigma-Aldrich. Nitric acid (HNO_3 , 65%), triethanolamine (TEA, >98.5%) and tetraethyl ammonium hydroxide (TEAOH, 35%), tetraethyl orthosilicate (TEOS, 98%), and tetradecane (>99.5%) were purchased from Fluka. Pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) and Pluronic F127 ($\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$) were purchased from BASF. All chemicals were used as received without any further purification.

3.2.2 Synthesis of SBA-16

3.2.2.1 Method 1

SBA-16 mesophases was first synthesized following the procedure reported by Zhao and coworkers, where Pluronic F127 was used as structure-directing agent [13]. 4 g of F127 was dissolved in 30 g of deionized water and 120 g of 2M HCl at 313 K. 8.5 g of TEOS was slowly added into the solution followed by stirring at the same temperature for 20 h. The solution was aged at 353 K overnight without stirring before the solid product was recovered, washed and dried under ambient conditions.

3.2.2.2 Method 2

In the 2nd synthesis procedure, NaCl/HCl solution was introduced as an additive [14]. 4 g of F127 copolymer and 14.10 g of NaCl were dissolved in 160 mL of 0.5 M HCl at 313 K under vigorous stirring for 4 h. 16.8 g of TEOS was added dropwise to the above solution. The resulting mixture was stirred for 20 h followed by hydrothermal treatment at 373 K for 24 h under static conditions in a Teflon-lined sealed container. The precipitation was filtered, washed with deionized water and dried at 353 K. The powder product was extracted with a mixture of 200 mL of EtOH (95 vol%) and 4 mL of HCl (37 wt.%) at 333-343 K for 24 h. After drying at 353 K, the sample was calcined at 823 K in air for 4 h.

3.2.2.3 Method 3

The 3rd synthesis procedure is as follows [15]: 5 g of F127 was dissolved in 240 g of deionized water and 10.5 g of HCl (37 wt.%). After complete dissolution, 17.5 g of BuOH was added at 318 K and stirred for 1 h, followed by adding 21.5 g of TEOS. The mixture was further stirred vigorously at 318 K for 24 h. The molar composition of the reaction mixture was designed as 0.0035 F127/ 0.91 TEOS/ 2.08 BuOH/0.91 HCl/ 117 H₂O. Subsequently, the mixture is aged at 373 K for 24 h under static conditions in a polypropylene bottle. The precipitated product was filtered without washing and dried at 373 K. Template was removed by a brief washing using EtOH/HCl mixture, followed by calcination at 823 K in air.

3.2.2.4 Method 4

The preparation method reported by Son *et al.* was employed as the 4th one [16], where 4 g of F127 was dissolved in a mixture of 190 g of H₂O, 8.3 g of HCl and 12 g of BuOH at 318 K. 9 g of TEOS was added dropwise. The mixture was stirred at 318 K for 24 h followed by aging at 373 K for 24 h under reflux condition. The resultant mixture was filtered, washed several times with deionized water, dried, and calcined at 823 K for 6 h in air.

3.2.2.5 Method 5

During the 5th preparation procedure, 3 g of F127 copolymer was dissolved in a solution of 144 g of deionized water and 5.94 g of concentrated HCl and stirred for 30 min [17]. 9 g of BuOH was added to achieve a ternary synthesis mixture with 1F127/3BuOH mass ratio. The solution was stirred for 1 h followed by adding 14.2 g of TEOS. The mixture was further stirred at 318 K for 24 h before the hydrothermal treatment at 373 K for 48 h.

3.2.2.6 Method 6

In the last synthesis process, 0.47 g of P123 and 2.33 g of F127 were dissolved in a mixture of 24 g of deionized water and 113 g of 2 M HCl under stirring at room temperature [18]. 10.4 g of TEOS was added to this mixture and stirred for another 20 h at 310 K. The molar composition of synthesis mixture was: 1 TEOS: 0.0016 P123: 0.0037 F127: 4.4 HCl: 143 H₂O. Hydrothermal treatment was carried out at 373 K for 48 h.

3.2.3 Synthesis of TUD-1

TUD-1 was synthesized following the hydrothermal method reported by Quek et al. [19], using TEA and TEOS as template and silica precursor, respectively. The preparation procedures were as follow: 7.2 g of TEA and 1.8 g of deionized water were added dropwise to 10.0 g of TEOS under vigorous stirring. 10.1 g of TEOH was added as co-template after 30 min. The mixture was aged at room temperature for 24 h, dried at 373 K for 24 h, and hydrothermally treated in a Teflon-lined stainless steel autoclave at 453 K for 8 h. The final product was calcined at 873 K for 10 h in air to remove the template.

3.2.4 Synthesis of MCM-41

Mesoporous silica materials MCM-41 was synthesized following the method reported by Hu et al. [20]. In a typical synthesis process, 0.97 g of CTAB was dissolved in a mixture of 20 mL of NH₃ H₂O (25%) and 15 mL of deionized water. The surfactant solution was stirred till a clear solution was obtained. 4.5 g of TEOS was added dropwise under vigorous stirring. After additional stirring for 2 h, the synthesis gel was transferred into a Teflon-lined stainless steel autoclave and placed in an oven at 393 K for 48 h. After cooling to room temperature, the resulting powder was recovered by filtration, washed with deionized water and dried under ambient conditions.

3.2.5 Synthesis of SBA-15

The siliceous SBA-15 was synthesized following a well-established procedure under acidic conditions using TEOS and a tri-block copolymer as silica precursor and template, respectively [20]. 2 g of Pluronic P123 was dissolved in 12.5 mL of deionized water under vigorous stirring. Upon the dissolution of P123, 35 mL of 0.29 M HCl was added. The mixture was then stirred for 1 h at room temperature followed by adding 4.5 g of TEOS dropwise under stirring. After stirring at 313 K for 24 h, the white suspension was transferred into a polypropylene bottle and placed in an oven at 373 K for 24 h. The resulting powder was recovered by filtration, washed with deionized water and dried under ambient conditions.

3.2.6 Surface functionalization of mesoporous silica materials

In this thesis, mesoporous silica materials (MCM-41, SBA-15, SBA-16, and TUD-1) were successfully surface-functionalized with various organosilanes (APS, ATMS, HMDS, and MPTMS) via a post-synthesis grafting method, as illustrated in Scheme 3.1. In a typical preparation as exemplified by APS modified TUD-1, 1.0 g of TUD-1 was dispersed in 30 mL of toluene and refluxed at 383 K for 12 h under a N_2 flow of 50 mL min^{-1} . 1.2 mmol of APS was added to the suspension and stirred for another 5 h. The resulting powders were filtered, washed with toluene, and dried at 353 K to remove the residual solvent. The corresponding samples were denoted as APS-TUD.

Scheme 3.1 surface-functionalization of silica mesoporous materials with various organosilanes (APS, ATMS, HMDS, and MPTMS) via a post-synthesis grafting method.

3.2.7 Preparation of metal nanoparticles confined in the surface-modified silica mesoporous materials via adsorption-reduction method

Monometallic and bimetallic catalysts supported on surface-functionalized silica mesophases were prepared following a ship-in-a-bottle method reported by Sun *et al.* [21]. In a typical preparation (see Scheme 3.2), exemplified by Au catalysts supported on surface-functionalized SBA-16 (denoted as Au/APS-S16), certain amount of 2 wt.% $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solution was added to 0.2 g of APS-SBA-16, suspended in 20 mL deionized water, followed by vigorous stirring at 353 K for 5 h. The catalyst was obtained by filtering and washing with deionized water, and drying at 353 K overnight. The catalyst was pretreated in a H_2 flow of 20 mL min^{-1} at 673 K for 2 h to reduce metal cations to metallic nanoparticles.

Scheme 3.2 Preparation of metallic catalysts over surface-functionalized silica mesoporous supports via adsorption-reduction method.

3.2.8 Preparation of metal nanoparticles confined in SBA-15 via glow discharge plasma reduction

Plasma technologies have emerged as a promising catalyst preparation approach and been employed to successfully prepare effective catalysts with unusual chemical activities due to the plasma species involved in the catalyst surface reactions [22-23]. Compared to other conventional catalyst synthesis protocols, plasma approach exhibits the following advantages: (i) a higher dispersion and distribution of active species; (ii) reduced energy requirements; (iii) enhanced catalytic activity, selectivity and long-term stability; and (iv) shortened preparation time. There are three main trends in catalyst preparation using plasma: (i) plasma chemical synthesis of ultrafine particle catalysts; (ii) plasma assisted deposition of catalytically active compounds on various carriers, particularly plasma spraying for the supported catalyst preparation; and (iii) plasma enhanced preparation or plasma modification of catalysts. Among them, chemical treatment or modification of catalyst using glow discharge plasma has attracted more attention due to the low operating temperature (room temperature) and alternative reducing agents (non-hydrogen gases). In this thesis, the novel argon glow discharge plasma reduction was employed to prepare metal catalysts supported SBA-15 molecular sieves.

The SBA-15 mesoporous silica was synthesized in the laboratory of Prof. D.Y. Zhao (Department of Chemistry, Fudan University, P.R. China, $S_{\text{BET}} \approx 600 \text{ m}^2/\text{g}$, $d_{100} \approx 10 \text{ nm}$) [24] and calcined in air at 773 K for 3 h to remove the adsorbed water prior to use. The monometallic Au, Pd and bimetallic Au-Pd catalysts confined in SBA-15 were prepared via a conventional incipient-wetness impregnation method with aqueous solutions of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and/or $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. The nominal metal loadings are 2 wt.% for monometallic Au or Pd catalyst and 2 wt.% Au-2 wt.% Pd for Au-Pd bimetallic catalyst. The Ar glow discharge plasma pretreatment was applied to introduce the metal precursors into the SBA-15 pores and reduce them by the electrons within the plasma, following the glow discharge plasma setup and plasma reduction protocol previously reported [25-26]. Typically, the sample (about 0.4 g) was loaded on a quartz boat and placed in a quartz tube (i.d. 35 mm) with two stainless steel electrodes (o.d. 30 mm). When the pressure in the discharge tube was evacuated to about 100 Pa, the glow discharge plasma was generated by applying 1000 V to the electrodes using a high voltage amplifier (Trek, 20/20B). The signal input for the high voltage amplifier was supplied by a function/arbitrary waveform generator (Hewlett-Packard, model 33120A) with a 100 Hz square wave. Ultra high pure grade argon (> 99.999%) was used as the plasma-forming gas. The plasma reduction was operated for 10 min per cycle (8 cycles in total), with a manual mixing of the sample at intervals between the treatments to ensure even exposure to the plasma. The bulk temperature of the plasma was measured by infrared imaging (Ircon modes 100PHT) and close to room temperature, indicating the negligible heating effect of the glow discharge. The obtained catalysts were denoted as Au/S15-p, Pd/S15-p and AuPd/S15-p. For comparison, the impregnated AuPd/S15 catalyst was also reduced in a H_2 flow (purified H_2) of 20 mL min^{-1} at 673 K for 2 h,

and designated as AuPd/S15-H. To study the effect of post-treatment, AuPd/S15-p was subjected to re-oxidation in an O₂ flow of 30 mL min⁻¹ at 773 K for 3 h, followed by reduction in a H₂ flow (5 vol% H₂/He) of 60 mL min⁻¹ at 773 K for 4 h, and designated as AuPd/S15-pO and AuPd/S15-pR, respectively. The same post-treatment procedures were also applied to AuPd/S15-H, which is subsequently denoted as AuPd/S15-HR.

Figure 3.1 The apparatus for Ar glow discharge post-treatment of catalysts.

Scheme 3.3 Preparation of metallic nanoparticles confined in SBA-15 via glow discharge plasma post-reduction.

3.3 Catalyst evaluation

The solvent-free aerobic oxidation of benzyl alcohol with molecular O₂ was carried out using a bath-type reactor operated under atmospheric condition. Experiments were conducted using a three-necked glass flask (capacity: 25 mL) pre-charged with certain amount of benzyl alcohol and catalyst. The mixture was stirred using a magnetic stirrer and heated in a silicon oil bath. The system was

equipped with a thermocouple to control the temperature and a reflux condenser. In each reaction run, the mixture was heated to 433 K under vigorous stirring. Oxygen flow was bubbled into the mixture to initiate the reaction once the reaction temperature was reached. After the allowed reaction time, the mixture was quickly quenched for further extraction. The solid catalyst was filtered off and the liquid organic products were analyzed by an Agilent gas chromatograph 6890 equipped with a HP-5 capillary column (30 m long and 0.32 mm in diameter, packed with silicabased supel cosil) and flame ionization detector (FID). The injector temperature was 523 K and the split is 0.1 μL . The column head pressure of the carrier gas (helium) during the analysis was maintained at 22.57 psi. Temperature program: 373 to 393 K; 20 K min^{-1} ; hold for 3 min. The conversion of benzyl alcohol, the selectivity towards benzaldehyde and *quasi*-turn over frequency (*q*TOF) are defined as follows:

$$\text{conversion}(\%) = \frac{\text{moles of reactant converted}}{\text{moles of reactant in feed}} \times 100\%$$

$$\text{selectivity}(\%) = \frac{\text{moles of product formed}}{\text{moles of reactant converted}} \times 100\%$$

$$q\text{TOF}(\text{h}^{-1}) = \frac{\text{moles of reactant converted}}{\text{moles of total active sites} \times \text{reaction time}}$$

Several control experiments were carried out to examine the carbon balance. To ensure the reliability of the catalytic results (conversion and selectivity), tetradecane (C14) was used as inert standard for the selective oxidation of benzyl alcohol.

First, 50 mmol (5.407 g) of benzyl alcohol and 50 μL of C14 were mixed. 100 μL of the mixture was diluted with 1 mL of ethyl acetate (solvent) as a control sample and tested by gas chromatograph. Only three peaks are obtained: ethyl

acetate, benzyl alcohol and C14, respectively. Afterward, a new batch of reaction were carried out pre-mixed with 50 μL of C14, using AuPd/S15-p as catalyst. After 1 h, 100 μL of the mixture was diluted with 1 mL of ethyl acetate and tested by gas chromatograph. Six peaks are obtained: ethyl acetate, toluene, benzaldehyde, benzyl alcohol, benzoic acid and C14, respectively. Since the injected volume is consistent, the mass should be proportional to the peak intensity. Thus, mass of each compound is calibrated according the peak area. Besides the detection and analysis of the liquid phase output, the gas phase components also need examination. The boiling point of the major by-product toluene is 383 K, which is lower than reaction temperature (433 K). Although a reflux condenser is employed, the volatilization and emission of toluene is still possible and cannot be neglected. Moreover, the organic compounds may decompose to small molecule gases, such as CO and CO₂, under high reaction temperature. Therefore, the tail gas was collected with gas sampling bags and examined by gas chromatograph afterward.

After correction, the carbon balance is 98.5%, which may be due to a trace of carbonaceous materials (gaseous toluene, CO or CO₂) volatilized during the reaction. Therefore, the carbon loss can be neglected and the obtained catalytic results in this study are reliable.

This catalytic process is a typical slurry-phase reaction with one liquid reactant, a solid catalyst, and one gaseous reactant. For multiphase reaction, mass transfer effects are likely to mask the true kinetics of this reaction. In order to eliminate the external mass transfer limitation, the effect of stirring speed on benzyl alcohol conversion was studied. The plot in Figure 3.2 shows that the conversion initially increases with stirring, denoting a mass-transfer-controlled regime. Increasing the stirring rate would enhance the mixing between the liquid and gas phases in the

reaction mixture, contributing to a high availability of oxygen at the catalyst surface. When the stirring speed is above 1000 rpm, the conversion reaches a plateau, denoting a kinetics controlled regime. Thus, the stirring speed was set at 1000 rpm for all the experiments in this study.

Figure 3.2 Effect of stirring speed on conversion of benzyl alcohol over Au/SiO₂ at 433 K under molecular O₂ for 1 h.

The dependence of the benzyl alcohol oxidation on the catalyst amount was investigated for the range between 0-150 mg, by plotting the benzyl alcohol conversion versus the catalyst amount in the system (Figure 3.3). In the absence of catalyst, subtle activity was obtained due to non-heterogeneous catalysis. The activity increases with increasing catalyst amount and reached the maximum over 20 mg catalyst. Nevertheless, further addition of catalyst would lead to a deterioration of activity, which may be attributed to a depressed mixing between solid and liquid reactants. Thus, the catalyst amount was set at 20 mg in this study.

Figure 3.3 Effect of catalyst amount on conversion of benzyl alcohol over Au/SiO₂ at 433 K under molecular O₂ for 1 h.

Sufficient O₂ is indispensable to give a clean catalyst surface with free active sites by reacting with hydride intermediates to form H₂O and removing the surface impurities from in side-reactions, which consequently leads high benzaldehyde selectivity and good long-term stability. Moreover, surface oxygen may enhance the desorption of the desired product, benzaldehyde, preventing the secondary reaction of surface alkoxide [27]. However, overdose of O₂ can result in excessive oxygen coverage of the active sites that diminishes the catalytic activity, *i.e.*, catalyst deactivation. Thus, O₂ should be supplied appropriately, *i.e.*, facilitate the reaction as well as avoid the over-oxidation. The effect of gaseous O₂ flow rate on the benzyl alcohol oxidation is studied, as depicted in Figure 3.4. The conversion initially increases with O₂ flow rate, but gradually drops when O₂ flow is above 20 mL min⁻¹. Therefore, the O₂ flow rate was set at 20 mL min⁻¹ for all the experiments in this study.

Figure 3.4 Effect of oxygen flow rate on conversion of benzyl alcohol over Au/SiO₂ at 433 K for 1 h.

To exam the data accuracy, we repeated benzyl alcohol oxidation over a representative catalyst 1Pd/1.2APS-TUD five times at the following reaction conditions: benzyl alcohol, 50 mmol; benzyl alcohol/Pd = 250 mol/g; temperature, 433 K; reaction time, 1h; stirring rate, 1000 rpm. After calibration, the uncertainties are: conversion, $\pm 0.15\%$; selectivity, $\pm 0.35\%$; q TOF, $\pm 0.08\%$.

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Chapter 4 Solvent-free aerobic oxidation of benzyl alcohol over Pd monometallic and Au-Pd bimetallic catalysts supported on SBA-16 mesoporous molecular sieves

The selective oxidation of alcohols, particularly benzyl alcohol to benzaldehyde, is of paramount importance in transforming functional groups in organic synthesis. The corresponding aldehydes or ketones are valuable as both intermediates and high value products for the pharmaceuticals, agrochemicals, and perfumery industries [1-3]. Benzyl alcohol oxidation is also frequently employed as a model aromatic alcohol oxidation in the laboratory study due to its relatively high reactivity. Additionally, the main product benzaldehyde is a non-enolizable aldehyde, which reduces the number of possible by-products, and makes the explanation of reaction mechanism less susceptible. From the viewpoints of atom economy and environmental concern, tremendous effort was made to develop heterogeneous catalysts using transition metals as a “greener” alternative to replace the conventional stoichiometric process, which requires expensive additives and generates aqueous waste containing a large amount of inorganic salts [4-6].

The catalytic role of supported metals for selective oxidation of benzyl alcohol has been extensively studied [7-9]. Among various transition metals, gold and palladium catalysts have attracted significant attention due to their superior catalytic performance. Numerous literatures [10-20] have reported the investigation on Au and Pd heterogeneous catalysts since the first successful CO oxidation over Au by Haruta et al. [21] and the first application of Pd in catalyzing aerobic oxidation of alcohols by Blackburn and Schwartz [22]. The supported Pd and Au monometallic catalysts were highly effective for the oxidation of 1-phenylethanol under mild solvent-free conditions, giving a turnover frequency (TOF) of $9\ 800\ \text{h}^{-1}$ for Pd

supported on hydroxyapatite (Pd/HAP) [10] and $12\,500\text{ h}^{-1}$ for Au supported on cerium oxide (Au/CeO₂) [11]. More recently, Li et al. have reported that zeolite-supported Pd nanoparticles with a mean diameter of 2.8 nm possessed an extraordinary efficiency (TOF of $18\,800\text{ h}^{-1}$) for solvent-free 1-phenylethanol aerobic oxidation [23]. In this study, we carried out the solvent-free aerobic oxidation of benzyl alcohol, a less active aromatic alcohol compared to 1-phenylethanol, to examine the catalytic activities because the lower catalytic activity presented by less active reactant allows one to get more insight into the nature of catalyst and catalytic mechanism.

From both the scientific and technological point of views, bimetallic nanoparticles are of greater interest than monometallic ones for improving the catalytic properties due to the synergetic effect between two metal elements. Recently, several research groups have examined the supported Au-Pd bimetallic catalysts with remarkably enhanced catalytic activity and product selectivity in various alcohol oxidation reactions. Enache et al. demonstrated that Au-Pd/TiO₂ presented a unusually high TOF ($269\,000\text{ h}^{-1}$) for 1-phenylethanol selective oxidation, showing the combination of gold and palladium in an alloyed nanoparticles configuration led to a twenty five-fold improvement in the catalytic activity [24]. The advantage of bimetallic catalyst is attributed not only to the electronic interaction between two metals but also to the complex structure of the bimetallic nanoparticle [25]. Several studies tested different bimetallic nanoparticle structures, such as core-shell structure [24, 26-32], cluster-in-cluster structure [33], and single alloy structure [34-38]. Lee et al. also reported a three-dimensional flower-shaped porous Au-Pd alloy nanoparticle with a Pd-enriched surface [39].

High surface area oxide supported metal nanoparticles show many interesting

catalytic behaviors. Among the support materials studied in catalytic reactions, mesoporous silica, such as M41s and SBA series silicates have been demonstrated as good supports due to their high area ($\sim 1000 \text{ m}^2 \text{ g}^{-1}$), tunable pore sizes (2.0-10.0 nm) and uniform pore size distribution. In particular, SBA-16 is considered to be one of the most interesting mesostructures with a 3-D cubic arrangement of cage-like mesopores corresponding to the *Im3m* space group [40-44]. SBA-16 mesoporous silicas with thick pore walls and high thermal stability are usually synthesized in a low-pH solution [45]. The important applications of SBA-16 include catalyst support, template for nanostructure synthesis, materials to immobilize or adsorb biomolecules [46]. Our recent investigation on Au catalysts supported on SBA-16 showed high activity in the solvent-free benzyl alcohol selective oxidation with molecular oxygen [47].

In this chapter, we report the synthesis, characterizations and catalytic tests of a series of Pd monometallic and Au-Pd bimetallic catalysts supported on SBA-16. Despite the advances developed in studying the size-dependent effect of noble metal nanoparticles, there is still a notable lack of chemistry of metal-support interactions. In this study, the effect of surface chemistry on the catalytic activity will be tackled by decorating the SBA-16 surface with different functional groups. The correlation between catalytic activity and metal nanoparticles confinement, *e.g.*, structure and morphology, of these Au-Pd bimetallic catalysts will also be discussed.

4.1 SBA-16 support

Pristine SBA-16 was synthesized via six different methods in Section 3.2.2 and compared by careful characterizations to figure out the best synthesis method.

X-Ray diffraction, which is one of the most important techniques for characterizing the structure of crystalline or other ordered materials, has been

widely used in the study of mesoporous silica materials. Poorly resolved XRD patterns were observed for samples obtained via synthesis methods 1, 2, 4, 6. The low angle XRD patterns for the pristine SBA-16 sample synthesized using method 3 and 5 are illustrated in Figure 4.1a. For SBA-16 synthesized by method 3, one intense diffraction peak and two higher angle peaks can be clearly observed in the range of $2\theta = 0.8^\circ$ - 2.0° , which are assigned as (110), (200) and (211) planes, indicating the well developed and highly ordered cubic mesoporous structure. By using Bragg's Law, the d -spacing of (110) plane calculated is ca. 10 nm. However, for SBA-16 synthesized by method 5, only one weak diffraction peak centered at $2\theta = 0.8^\circ$ appears obviously and the other two high angle peaks become less resolved, which indicates a poorly ordered mesostructure. Therefore, method 3 was applied to synthesize all the pristine SBA-16 samples through the whole work.

Figure 4.1 (a) XRD patterns for SBA-16 synthesized by methods 3 and 5, (b) TEM images of SBA-16 synthesized by method 3.

Transmission electron microscopy (TEM) images, inserted in Figure 4.1b, were taken to directly observe the mesoporous structure of pristine SBA-16. The

TEM images, which are assigned to the projection of (110) and (111) plane respectively, identify the highly ordered body-centered cubic mesostructure of synthesized SBA-16 with $Im\bar{3}m$ space group. Furthermore, the distance between two adjacent SBA-16 mesopores is ca. 9 nm, which is in good agreement with the calculated result from XRD patterns.

Compared to the XRD characterization, nitrogen physisorption provides the bulk-averaged information of the mesoporous materials. In this study, nitrogen physisorption was conducted to complement XRD measurement, determining the structure, surface area, pore size and volume of the synthesized SBA-16. Figure 4.2 shows the nitrogen adsorption-desorption isotherms and pore size distribution of SBA-16. The plots obtained are typical type IV isotherms with a pronounced hysteresis loop characteristics for cage-like materials with interconnected uniform mesopores [48]. The synthesized SBA-16 exhibits a BET surface area of $950 \text{ m}^2 \text{ g}^{-1}$, pore volume of $0.7 \text{ cm}^3 \text{ g}^{-1}$, and a narrow pore size distribution centered at 3.7 nm for the desorption branch and 6.7 nm for the adsorption branch, which are in good agreement with the results reported elsewhere [42].

Figure 4.2 N_2 physisorption isotherms of SBA-16 synthesized by method 3 and pore size distribution calculated from the desorption branch by BJH method.

4.2 Catalytic performance of Au monometallic catalysts

SBA-16 with “super-cage” pore structure is proposed to be a superior stabilizer to confine metal nanoparticles with a narrow size distribution in a ship-in-a-bottle way. Therefore Au/SBA-16 was synthesized under different conditions and the catalytic results for solvent-free benzyl alcohol selective oxidation with molecular O₂ are listed in Table 4.1.

In Table 4.1, the SBA-16 sample pretreated in a H₂ flow at 673 K showed the best catalytic performance with benzyl alcohol conversion of 19.0% and TOF of 2419 h⁻¹. For comparison, the catalytic performances of Au/SBA-15 and Au/MCM-41 catalysts with the same Au content (ca. 1 wt.%) are also investigated. Both Au/SBA-15 and Au/MCM-41 successfully catalyzed the benzyl alcohol oxidation at 413 K, producing benzaldehyde as the main product. However, both benzyl alcohol conversion and TOF are lower than that of Au/SBA-16.

Table 4.1 Catalytic results of benzyl alcohol oxidation over Au-containing mesoporous silica catalysts^a.

Catalyst	Pre-treatment	Conv.(%)	Benzaldehyde select. (%)	TOF(h ⁻¹)
SBA-16	-	< 1.0	-	-
Au/SBA-16-80	Air, 353 K	6.3	> 99	803
Au/SBA-16-540	Air, 813 K	3.8	> 99	484
Au/SBA-16-200H	H ₂ , 473 K	13.0	> 99	1655
Au/SBA-16-400H	H ₂ , 673 K	19.0	> 99	2419
Au/SBA-15-400H	H ₂ , 673 K	16.1	> 99	2048
Au/MCM-41-400H	H ₂ , 673 K	6.5	> 99	827

^a Reaction conditions: the amount of Au in each catalyst, 2.5×10⁻³ mmol; benzyl alcohol, 10 mL; O₂, 20 mL min⁻¹; temperature, 413 K; reaction time 3 h.

To figure out the structure of Au catalysts and reveal the correlation between Au nanoparticles and different supports, UV-Vis and TEM measurements were introduced to carefully examine the Au catalysts.

The UV-vis spectra of Au-containing mesoporous silica catalysts pretreated in a H₂ flow at 673 K are shown in Figure 4.3. All samples show the characteristic surface plasmon resonance (SPR) absorption peak of Au nanoparticles at around 520 nm. Compared to Au/SBA-16, Au/SBA-15 and Au/MCM-41 exhibit a slightly red-shifted and a narrower absorption band, indicating a larger mean particle size and more particle aggregation.

Figure 4.3 UV-Vis spectra of Au-containing mesoporous silica samples: (a) Au/SBA-16; (b) Au/SBA-15; (c) Au/MCM-41.

TEM observation was performed to examine the Au nanoparticle size, as shown in Figure 4.4. Obviously, Au nanoparticles are homogeneously distributed in the size range of 2-9 nm in Au/SBA-16. The particles have a maximum of size distribution at 5-6 nm and those larger than ca. 7 nm can hardly be observed in this sample. Considering the unique interconnect mesoporous structure of SBA-16, it is reasonable to conclude that most of Au nanoparticles are confined inside the cage of SBA-16 structure. However, relatively large Au nanoparticles with sizes more than ca. 7 nm were observed in Au/SBA-15 and Au/MCM-41 catalysts, indicating Au

nanoparticles are not well confined in the pore structure of SBA-15 and MCM-41 and many large particles may be stabilized outside of the pores. Moreover, Au particles over SBA-15 and MCM-41 display much broader size distribution than that of SBA-16. Therefore, it is obvious that SBA-16 shows excellent superiority to SBA-15 and MCM-41 to confine Au nanoparticles due to its unique pore structure. Combined the catalytic performances of Au-containing samples discussed above, we proposed that the Au nanoparticles with a mean size of 5-6 nm confined within the SBA-16 cage are more active for benzyl alcohol oxidation with molecular O₂.

Figure 4.4 TEM micrographs and particle size distributions of Au-containing mesoporous silica samples: (a) Au/SBA-16, (b) Au/SBA-15, (c) Au/MCM-41.

4.3 Catalytic performance of Pd monometallic catalysts

Table 4.2 lists the results of solvent-free benzyl alcohol selective oxidation with molecular O₂ over Pd monometallic catalysts. The catalytic performances of SBA-16 supported Pd are benchmarked with Pd/SiO₂ and Pd/Al₂O₃, considering that SiO₂ and Al₂O₃ are also common and effective supports for benzyl alcohol oxidation using noble metals. The reaction of benzyl alcohol with molecular oxygen over Pd produces benzaldehyde as the main product along with toluene and trace amount of benzoic acid as the byproducts. Pd/Al₂O₃ exhibits the highest conversion of 43.3% and TOF of 11 534 h⁻¹ at 413 K, which are twice of Pd supported on silica supports, regardless of SiO₂ or SBA-16. However, the selectivity towards benzaldehyde is rather low over Pd/Al₂O₃ with a tremendous amount of toluene as byproduct. Enche et al. suggested the acidic nature of Al₂O₃ support likely led to the byproduct formation [24]. Pd/SiO₂ shows lower conversion compared to Pd/Al₂O₃, but the benzaldehyde selectivity is improved, suggesting that silica support can effectively inhibit the production of toluene. When SBA-16 and surface modified SBA-16 are employed as supports, the selectivity towards benzaldehyde remarkably increases. It is interesting to note that the conversion and TOF over Pd supported on surface modified SBA-16 (both APS and HMDS) are more than twice of the results of Pd supported on pristine SBA-16.

Table 4.2 Catalytic results of benzyl alcohol oxidation over Pd monometallic catalysts on different supports^a.

Catalyst	Conversion (%)	Selectivity(%)			TOF (h ⁻¹)
		Benzaldehyde	Toluene	Benzoic Acid	
Pd/S16	9.5	90.2	7.2	2.6	3701
Pd/HMDS-S16	20.3	89.8	10.2	0.0	7727
Pd/APS-S16	21.0	94.6	5.0	0.4	7858
Pd/SiO ₂	22.7	82.9	17.1	0	6027
Pd/Al ₂ O ₃	43.3	64.9	34.9	0.2	11534

^a Reaction conditions: catalyst, 20 mg; benzyl alcohol, 50 mmol; O₂, 20 mL min⁻¹;

temperature, 413 K; reaction time, 1 h.

Different functional groups can be effectively grafted onto the mesopore wall surface of pristine SBA-16 by using an appropriate silane modifier to react with Si-OH groups on the internal pore wall surfaces. The catalytic performances of Pd supported on functionalized SBA-16 can be ultimately explained from the nature of the support surface. Romanmartinez et al. proposed that the dispersion of metal precursor on the support and the metal-support interaction were strongly dependent on the nature of the support, *i.e.*, the support surface chemistry [49]. Substitution of the surface silanol groups with other functional groups facilitates the diffusion and adsorption of metal precursor, resulting in a remarkably different dispersion of Pd on the support surface. The pristine SBA-16 surface is mildly acidic and negatively charged because of the hydrolysis of –OH groups, which is a barrier for the diffusion and adsorption of negatively charged $\text{PdCl}_2(\text{OH})_2^{2-}$ species hydrolyzed by PdCl_2 . The neutrally charged surface of HMDS-S16 only decreases the barrier for the diffusion of negatively charged $\text{PdCl}_2(\text{OH})_2^{2-}$ precursors. Therefore, in the case of both pristine and HMDS-modified SBA-16, there is no strong affinity between the palladium precursor and the support, resulting in an unsatisfactory Pd dispersion. APS-S16 surface is positively charged due to the hydrolysis of –NH₂ groups which exhibits a great affinity to the negatively charged $\text{PdCl}_2(\text{OH})_2^{2-}$. The palladium precursor can be easily adsorbed into the mesochannels of SBA-16 due to the enhanced metal precursor-support interaction, leading to a uniform Pd nanoparticle dispersion. Pd/APS-S16 also shows the highest benzaldehyde selectivity (94.6%) towards desired benzaldehyde due to the elevated surface basicity which is beneficial to the dehydrogenation of benzyl alcohol [50]. Similar effect of surface basicity on the catalytic activity has also been discovered in the CO oxidation [51]

and the propane oxidative dehydrogenation [52]. APS-S16 was chosen as the support in the following work because Pd/APS-S16 presented the highest benzaldehyde selectivity and reasonably good conversion of benzyl alcohol.

The catalytic performances of Pd/APS-S16 catalysts with various Pd loadings were investigated and the results are shown in Figure 4.5. All these catalysts show a high and constant selectivity towards benzaldehyde (>90%) but fail to give a distinct trend with the Pd loading, suggesting the benzaldehyde selectivity is only weakly affected by the metal loading but mainly dependent on reaction conditions as suggested by Haider et al. [53]. The benzyl alcohol conversion increases with Pd loading when the Pd loading is less than 2 wt.%, which is due to the increasing number of active sites available participating the reaction. The conversion slightly declines when the Pd loading is 3 wt.%, implying that high metal content may lead to the agglomeration of Pd metal nanoparticles. The formation of large clusters decreases the number of the available active sites for the reaction as suggested by Lee et al. [39]. TOF decreases monotonically with increasing the Pd loading and 0.5Pd/APS-S16 exhibits the highest TOF of $9\,015\text{ h}^{-1}$.

Figure 4.5 Catalytic performance of Pd/APS-S16 with various Pd loadings.

Reaction conditions: catalyst, 20 mg; benzyl alcohol, 50 mmol; O₂, 20 mL min⁻¹; temperature, 413 K; reaction time, 1 h.

4.4 Catalytic performances of Au-Pd/APS-SBA16 bimetallic catalysts

The effect of Au:Pd molar ratios on the catalytic activity of benzyl alcohol selective oxidation is shown in Table 4.3. Au/APS-S16 monometallic catalyst exhibits an extremely low conversion and benzaldehyde selectivity, with a large amount of toluene as byproduct. Partially replacing Au with Pd to form the bimetallic catalyst remarkably increases both the catalytic activity (conversion and TOF) and the selectivity towards benzaldehyde. The benzyl alcohol conversion increases with the Pd:Au molar ratio and reaches the maximum of 22.3% over 1Au5Pd/APS-S16 catalyst (TOF of 8 667 h⁻¹) which is higher compared to both Au and Pd monometallic catalysts. Such enhancements of catalytic activity have previously been observed for several Au-Pd bimetallic systems [37, 54-55]. The improved catalytic performance was suggested due to the positive synergistic electronic effects upon the addition of Pd into Au in which Au atoms draws electron

density away from Pd atoms, thereby enhancing the interaction of Pd atoms with the substrate [37, 54, 56].

Table 4.3 Effect of Au:Pd molar ratio on catalytic activity of benzyl alcohol selective oxidation^a.

Catalyst	Metal content (wt.%) ^b		Real molar ratio (Au:Pd)	Conv. (%)	Selectivity (%)			TOF (h ⁻¹)
					Benzaldehyde	Toluene	Benzoinic Acid	
Au/APS-S16	Au	0.89	1:0	2.5	86.1	13.9	0	1937
3Au1Pd/APS-S16	Au	1.15	1:0.4	13.1	89.3	10.7	0	4052
	Pd	0.24						
1Au1Pd/APS-S16	Au	0.97	1:0.7	15.5	94.0	6.0	0	4715
	Pd	0.35						
1Au2Pd/APS-S16	Au	0.71	1:1.1	19.6	94.1	5.3	0.6	6575
	Pd	0.41						
1Au3Pd/APS-S16	Au	0.40	1:2.5	22.3	91.3	8.2	0.5	7864
	Pd	0.54						
1Au5Pd/APS-S16	Au	0.24	1:4.2	22.1	94.4	4.8	0.8	8667
	Pd	0.55						
Pd/APS-S16	Pd	0.71	0:1	21.0	94.6	5.0	0.4	7858

^a Reaction conditions: catalyst, 20mg; benzyl alcohol, 50mmol; O₂, 20mL min⁻¹; temperature, 140 °C; reaction time, 1h.

^b metal content was tested by ICP.

When Pd monometallic and Au-Pd bimetallic nanoparticles were employed for the oxidation, benzaldehyde was preferentially produced with the selectivity greater than 90%, which is higher than that of Au monometallic nanoparticles. This variety has also been reported in other previous works [57-58]. The high selectivity towards benzaldehyde over the bimetallic catalysts does not show a distinct trend as the Au:Pd ratio varies, implying the benzaldehyde selectivity is weakly correlated to the metal composition as well [53]. Adding Pd into Au dramatically decreases the toluene selectivity. As suggested by Li [59] and Enache [60], toluene mainly comes from the disproportionation of benzyl alcohol via either a hydrogen transfer step or an oxygen transfer step. Corma and co-workers also suggested that Au-H and Pd-H species formed on supported Au and Pd catalysts are important in the toluene

formation [61-62]. Hence we attribute the distinct trend of toluene formation to the effectively weakened hydrogenation/dehydrogenation activity of Au-Pd bimetallic nanoparticles and the decreased number of Au-H and Pd-H species on the amine-functionalized surface of SBA-16. Nevertheless, the improvement by adding Au on Pd-SBA-16, which is not as distinct as we expected, can be attributed to either the structure of the synthesized bimetallic nanoparticles or the reaction limiting step in a liquid phase reaction over catalysts with mesoporous channels.

The temperature effect on the solvent-free benzyl alcohol selective oxidation was examined using 1Au3Pd/APS-S16, 1Au5Pd/APS-S16, Au/APS-S16 and Pd/APS-S16 catalysts. Figure 4.6 shows the conversion, selectivity and TOF at different temperatures (413, 393, and 373 K). The elevated reaction temperature leads to the increase in both conversion and TOF for all the catalysts as expected. The effective activation energies are determined using an Arrhenius plot. The effective activation energy for 1Au5Pd/APS-S16 catalyst is measured as ca. 16.7 kJ/mol, which is slightly higher than monometallic Au/APS-S16 (16.1 kJ/mol), Pd/APS-S16 (12.3 kJ/mol) and bimetallic 1Au3Pd/APS-S16 (15.5 kJ/mol). The low apparent activation energy implies that the catalytic activity of these catalysts has a low dependency on temperature; thus, it is unlikely to significantly increase the benzyl alcohol conversion by increasing the temperature. The calculated activation energies are much lower than the results of TiO₂ supported Au-Pd catalysts reported by Enache et al. (45.8 kJ/mol) [24], implying the alcohol oxidation is likely to be mass-transfer limited and controlled by the diffusion of reactants in the mesoporous channels under the reaction conditions in this study [63]. This mass-transfer resistance, to some extent, may lower the catalytic performance of the bimetallic catalysts. Such mass-transfer limitation also exists in other reported systems [64].

Interestingly, the benzaldehyde selectivity monotonically increases for Au/APS-S16 catalyst and remains constant for 1Au3Pd/APS-S16, 1Au5Pd/APS-S16, and Pd/APS-S16 catalysts. The origin of this selectivity trend is still under investigation.

Figure 4.6 Effect of reaction temperature on catalytic activity. Reaction conditions: catalyst, 20 mg; benzyl alcohol, 50 mmol; O₂, 20 mL min⁻¹; reaction time, 1 h.

4.5 Characterization of Au-Pd bimetallic catalysts

Several characterization techniques were employed to reveal the insights of catalyst nature. The N₂ physisorption isotherms of used 1Au5Pd/APS-S16 in Figure 4.7 show a clear step increase in nitrogen uptake but a distorted hysteresis loop, suggesting a less regular organization at long-range order of the mesoporous structure, arising from either the incorporation of metal particles into the channels or

the collapse of SBA-16 mesopores. The TEM image clearly shows that the long range array of mesoporous channels of SBA-16 is well sustained, ruling out the possibility of mesopores collapse and suggesting the good stability of SBA-16.

Figure 4.7 N₂ physisorption isotherms and pore size distributions for used 1Au5Pd/APS-S16, and inset of TEM image.

Figure 4.8 shows representative UV-vis absorption spectra of reduced Au, Pd monometallic and Au-Pd bimetallic catalysts. The monometallic Pd nanoparticles only show a broad absorption over the entire spectral range. The monometallic Au exhibits a characteristic surface plasmon resonance (SPR) absorption peak at 530 nm, which is attributed to Au nanoparticles having a size less than 10 nm [38]. No distinct SPR absorption peak can be detected for all the bimetallic catalysts because the presence of group 10 metal suppresses the SPR bands of group 11 metal [65-66]. The diminished plasmon band in the UV-vis spectra is attributed to the change in the

band structure of Au when interacts with Pd, which is consistent with the suggestion by Deki et al. [67]. These UV-vis results do not directly suggest the structure of the bimetallic active site, but imply the existence of alloying interaction between Au and Pd other than segregated monometallic clusters [27, 38, 58, 65-66]. Moreover, the absence of SPR absorption peaks at 310 and 407 nm assignable to unreduced Au^{3+} and Pd^{2+} cations suggests the complete reduction of Au and Pd precursors in the bimetallic catalyst system [39].

Figure 4.8 UV-Vis absorption spectra of APS-S16 supported catalysts with various Au/Pd molar ratios.

No diffraction peak can be observed using high angle XRD characterization except a broad diffraction peak at around $2\theta = 20^\circ$ which denotes the characteristic amorphous silica framework with no crystalline structure (not shown here),

implying the highly dispersed nature of these metallic nanoparticles supported on APS-S16. The direct TEM microscopic observation was performed to exam the mean particle size and the particle size distribution of APS-SBA16 supported catalysts with various Au:Pd molar ratios. The TEM micrographs of Au/APS-S16, Pd/APS-S16, 1Au3Pd/APS-S16 and 1Au5Pd/APS-S16 catalysts and the corresponding particle size distributions derived from counting ca. 150 particles are exhibited in Figure 4.9. The nanoparticles are uniformly dispersed and embedded in the mesoporous structure of SBA-16. The mean diameters of the monometallic Au and Pd nanoparticles are found to be 6.0 and 2.8 nm, respectively, suggesting that SBA-16 structure effectively encapsulates metal nanoparticles. Au-Pd bimetallic nanoparticles are also well confined in the mesochannels with slightly wider particle size distributions. Their mean diameters are 6.2 and 6.1 nm for 1Au3Pd/APS-S16 and 1Au5Pd/APS-S16, respectively, which are coincident with the inner diameter of SBA-16 super-cage. All these results suggest that the “super-cage” porosity of SBA-16 is superior for confining both monometallic and bimetallic nanoparticles in a “ship-in-a-bottle” way. The well-confined nanoparticles (mean size of 6 nm) are highly active in solvent-free benzyl alcohol selective oxidation with molecular oxygen. We also noted that the larger number density of the large particles may attribute to the origin of enhanced catalytic activity, that is, higher catalytic performance is associated with the presence of larger particles, which is also suggested by Hutchings et al [6].

Figure 4.9 TEM micrographs and particles size distributions of APS-S16 supported catalysts: (a) Au/APS-S16, (b) 1Au3Pd/APS-S16, (c) 1Au5Pd/APS-S16, (d) Pd/APS-S16.

The size-dependent effect has been extensively studied and proved to be a significant factor combined with metal-metal interaction and metal-support interaction in determining the catalytic activity [68-69]. In most previous studies of

bimetallic catalytic systems, the bimetallic nanoparticles with different metal composition usually possess different mean particle sizes and size distributions [27, 39, 58], resulting in an ambiguous explanation on the experimental results. In this study, we successfully exclude the size effect by controlling the bimetallic nanoparticles in a specific size range in the amine-functionalized SBA-16. As suggested in TEM results, the bimetallic nanoparticles are maintained in the same mean cluster size (ca. 6 nm) and reasonable consistent particle size distribution. Therefore, it should be more accurate to elucidate the effect of the metal-metal interaction and metal-support interaction on the catalytic activity.

High-resolution TEM (HRTEM) is indispensable for metal nanoparticle study not only on the particle size and shape but also on the crystallography information [70]. A HRTEM image of an individual Au-Pd bimetallic nanoparticle from 1Au5Pd/APS-S16 sample is shown in Figure 4.10a. Neither obvious phase contrast of boundary assignable to core-shell structure nor structural incoherency assignable to separate monometallic particles is observed. The nanoparticle exhibits a common decahedral multiply twinned structure, as indicated by the straight lines in Figure 4.10a [37, 71]. Moreover, it has been reported that Au-Pd bimetallic nanoparticle may maintain face-centered cubic (FCC) lattice structure when alloyed at almost any molar ratio [37]. The FCC lattice structure is discerned with 0.230 nm of the lattice spacing measured for the adjacent (111) plane, which is in between the values of Au (0.235 nm) and Pd (0.225 nm). This deviation of lattice constant causes the change of interatomic distance and therefore leads to both geometric and electronic effects, attributing to the unique chemical properties of bimetallic nanoparticles and the enhanced catalytic behaviors [37, 71]. These results further exclude the possibility of core-shell structure and segregated monometallic nanoparticles.

Figure 4.10 (a) HR-TEM image and (b) EDX intensity profile of a single 1Au5Pd/APS-S16 bimetallic nanoparticle.

We introduced EDX analysis, which is one of the most revealing methods for analyzing the composition of bimetallic nanoparticles, to examine the local metal compositions and element distribution in an individual bimetallic nanoparticle. EDX line scan was performed along the arrow for the representative individual bimetallic nanoparticle in Figure 4.10a and the intensity profiles of Au-L α and Pd-L α X-rays are plotted in Figure 4.10b. The intensity of each element is assumed to be proportional to the atomic densities. The bimetallic nanoparticle is not composed of single-phase alloy; Au is concentrated in the center while Pd is uniformly distributed over the entire scanning track. Combining the EDX analysis with UV-vis, XRD, and HRTEM results, the formation of Au core-Pd shell structure can be ruled out. The possible structure is that Pd clusters island on the surface of a relatively larger Au-rich core, which can be denoted as Pd cluster-on-Au cluster structure. Formation of bimetallic nanoparticles with such cluster-on-cluster structure has been reported, such as Pt-on-Ru [72] and Pd-on-Ag [73]. The formation of such Pd cluster-on-Au cluster structure is reasonable if we take the

redox potentials of these two elements into consideration. Au^{3+} has a higher redox potential (1.498 V) than that of Pd^{2+} (0.951 V); the higher positive the redox potential, the greater the affinity for electrons and more likely to be reduced. Therefore, the reduction of Au^{3+} is faster and metallic Pd is reasonably expected to be formed afterward, giving a Pd cluster-on-Au cluster structure rather than the reversed small Au cluster on Pd core structure previously reported [27]. During the formation of this cluster-on-cluster structure, Au^{3+} cations are reduced first to Au^0 atoms and constitute mainly the Au-rich core followed by the reduction of Pd^{2+} cations to Pd^0 atoms which uniformly disperse over the surface of Au clusters. This formation mechanism is similar to that has been proposed by Remita et al. for Au core-Pd shell alloyed cluster structure [74]. The formation of this unique bimetallic structure may also be due to the inter-metal electron interaction between Pd^0 atoms and Au^{3+} cations. Some Pd^{2+} cations may be reduced to Pd^0 atoms during the reduction of Au^{3+} cations, the metallic Pd^0 atoms are more prone to donate electrons to the residual Au^{3+} cations and reduce them to Au^0 atoms, where Pd^0 acts as the electron carrier for Au^{3+} reduction, resulting in the coagulation and atomic re-arrangement of the nanoparticles to form Pd cluster-on-Au cluster structure. As suggested by Toshima et al. [54], Pd has a larger tendency to occupy the shell than Au in the simultaneous reduction, leading to Pd enriched shell-Au enriched core structure. The structure of bimetallic nanoparticles can be changed by varying external factors, such as reduction sequence, solvent addition, and dose rate. Successive reduction of two metals is considered as one of the most suitable methods to form the desired bimetallic structure, therefore greatly affect the catalytic activity. Harada discovered that the clusters prepared by successive reduction starting from Au^{3+} ($\text{Au} \rightarrow \text{Pd}$) exhibited higher catalytic behavior than

those prepared by the reverse sequence (Pd→Au) [75]. It is suggested that the successive reduction of Au^{3+} and Pd^{2+} also plays a vital role in the enhanced catalytic performance of the bimetallic nanoparticles in this study. Nevertheless, these surface-enriched Pd clusters may not have a uniform distribution of active metal phase which may attribute to the less distinct enhancement of catalytic performance as that in the Au core-Pd shell structure reported by many researchers.

This Pd cluster-on-Au cluster structure was further evidenced by STEM-EDX mapping shown in Figure 4.11. The digitally colored STEM-EDX mapping image of an individual bimetallic nanoparticle shows that Au (yellow) locates predominantly in the center of the particle while Pd (purple) mainly distributes over the surface of Au-rich cluster, which complements the EDX line scanning results that the bimetallic nanoparticle is composed of two metal elements and constructed of Pd cluster-on Au cluster structure. This Pd cluster-on-Au cluster structure is expected to have a large amount of surface-exposed Pd atoms and therefore a high Pd surface area, which attributes to a high catalytic activity as suggested by He et al. [73].

Figure 4.11 High-magnification STEM image of an individual 1Au5Pd/APS-S16 nanoparticle and its STEM-EDX mapping images: (b) Au mapping image, (c) Pd mapping image, (d) overlap image of Au and Pd mapping.

4.6 Recycling test of bimetallic catalyst

An important factor that has to be taken into consideration is the catalytic stability. The metallic components of less stability easily leach out, resulting in either the formation of an active homogeneous catalyst or a loss in catalyst activity on subsequent recycling. The recycling tests of 1Au5Pd/APS-S16 catalyst were studied; the catalyst was recovered after each reaction run, washed with acetone, dried at 333 K and re-used in a subsequent new catalytic run. The total amount of catalyst was maintained at 20 mg by adding used catalyst. Figure 4.12 shows the recyclability of 1Au5Pd/APS-S16 for five cycles. It is noteworthy that the conversion and TOF slightly drop while the selectivity towards benzaldehyde

increases. This verifies that no observable leaching of Au and/or Pd from the catalyst occurs, indicating this bimetallic catalyst possesses long-term stability. The Au and Pd content after five reaction cycles are almost the same as those of the fresh catalyst; Au and Pd cannot be detected by ICP analysis in the filtrate after the reaction. Moreover, negligible conversion of benzyl alcohol is observed when the liquid filtrate is used as catalyst instead of the solid catalyst for further reaction. Hence, Au-Pd bimetallic catalysts do not only improve the catalytic activity and selectivity, but also enhance the resistance to deactivation, as suggested in other reports [24, 58, 71].

Figure 4.12 Recycling ability of 1Au5Pd/APS-S16 catalyst in solvent-free selective oxidation of benzyl alcohol with molecular oxygen. Reaction conditions: catalyst, 20 mg; benzyl alcohol, 50 mmol; O₂, 20 mL min⁻¹; temperature, 413 K, reaction time, 1 h.

4.7 Catalytic performance of bimetallic catalyst on various aromatic alcohols

In this study, 1Au5Pd/APS-S16 was selected to catalyze several aromatic alcohols and the results are listed in Table 4.4. 1Au5Pd/APS-S16 exhibits high

catalytic activity in the oxidation of 1-phenylethanol. After 1 h reaction, 38% of the substrate is oxidized solely to acetophenone, giving a significantly high TOF of 14 848 h⁻¹. After 6 h, 1-phenylethanol almost completely converts. Similar catalytic activity is observed in the oxidation of cinnamyl alcohol. The conversion reaches 32.8% after 1 h with TOF of 12 852 h⁻¹ and almost 100% after 12 h. In the oxidation of *p*-methylbenzyl alcohol and *p*-methoxybenzyl alcohol, although the initial oxidation rate is low with conversions of 17.4% and 6.8% respectively, both can largely be converted to the corresponding aldehydes after a period of reaction time. The bimetallic catalyst shows a poor catalytic activity in the oxidation of *p*-nitrobenzyl alcohol and *p*-bromobenzyl alcohol even after long time reaction. The Au-Pd bimetallic catalyst shows higher catalytic activity for substituted aromatic alcohols containing electron-donating group (*e.g.* -CH₃ and -CH₃O) than those containing electro-withdrawing groups (such as -NO₂ and -Br), which is consistent with the results reported previously [50].

Table 4.4 Catalytic properties of 1Au5Pd/APS-S16 in the oxidation of various alcohols with molecular O₂^a.

Substrate	Product	Time(h)	Conversion (%)	Selectivity (%)	TOF (h ⁻¹)
1	22.3	91.3	8667
1	38.0	100	14848
		3	77.9	100	10158
		6	97.1	100	6332
1	17.4	100	6812
		3	29.7	100	3878
		6	35.5	100	2313
		12	45.8	100	1496
		24	69.4	100	1132
1	6.8	100	2668
		3	13.6	100	1781
		6	24.5	100	1597
		12	50.2	100	1639
		24	92.9	100	1515
1	32.8	100	12852
		3	56.0	100	7309
		6	74.7	100	4870
		12	92.7	100	3023
1	1.2	100	470
		3	1.9	100	247
		6	2.1	100	131
1	0.8	100	316
		3	0.9	100	112
		6	1.7	100	110

^a Reaction conditions: catalyst, 20 mg; benzyl alcohol, 50 mmol; O₂, 20 mL min⁻¹; temperature, 413 K; reaction time, 1 h.

4.8 Conclusions

Highly ordered SBA-16 silica material with cage-like mesopores was synthesized and employed to effectively confine the formation of Au-Pd bimetallic nanoparticles. Surface-functionalization of SBA-16 showed great impact on the

catalytic performance and APS-functionalized SBA-16 was selected as the best support. The UV-vis, TEM, HRTEM, EDX, STEM-EDX analysis suggested the formation of alloyed bimetallic nanoparticles with Pd cluster-on-Au-cluster crystalline structure. These highly dispersed Au-Pd bimetallic nanoparticles with the mean diameter around 6 nm showed excellent catalytic performance in catalyzing the selective solvent-free oxidation of a variety of aromatic alcohols and maintained good catalytic stability after recycling. This work has been published in *Applied Catalysis A: General* (Chen et al. *Applied Catalysis A: General*, 2010, 380 (1-2), 55-65, 10.1016/j.apcata.2010.03.026), reuse in this chapter is under the permission of Elsevier Global Rights Department.

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Chapter 5 Surface-functionalized TUD-1 mesoporous molecular sieve supported palladium as a superior catalyst for solvent-free aerobic oxidation of benzyl alcohol

Making aldehydes or ketones from the selective oxidation of corresponding alcohols, in particular benzaldehyde from benzyl alcohol is regarded as one of the most versatile and powerful reactions in organic synthesis on both the laboratory and industrial scales. The catalytic roles of heterogenized noble metal (Pd, Au, Pt, Ru) catalysts in the aerobic oxidation of benzyl alcohol have been extensively investigated due to their superior catalytic performance relative to non-noble metals [1]. Among these noble metals, palladium catalysts have attracted considerable attention and been intensively studied. Numerous authors have reported the investigations on Pd-heterogeneous catalysts since the first successful Pd catalyzed aerobic oxidation of secondary alcohols [2]. Mori et al. showed that supported Pd catalysts are highly effective for the oxidation of 1-phenylethanol under mild solvent-free conditions, showing a turnover frequency (TOF) of $9\,800\text{ h}^{-1}$ for Pd supported on hydroxyapatite (Pd/HAP) [3]. Li et al. reported that zeolite-supported Pd nanoparticles with a mean diameter of 2.8 nm exhibited an extraordinary TOF of $18\,800\text{ h}^{-1}$ for 1-phenylethanol oxidation [4].

A strong alkaline medium is beneficial for certain reactions; and it has been demonstrated that gold alone cannot catalyze alcohol dehydrogenation in the absence of a strong base [5]. Basicity also plays a crucial role in the selective oxidation of alcohols, especially for primary alcohols. Precisely controlling the alkaline pH level in the reaction solution is vital to enhance the reaction by facilitating the reactant adsorption and product desorption, leading to a good-to-excellent selectivity [6]. Alternatively, base can be added to a

heterogeneous catalyst as the promoter, enhancing the hydrogen abstraction from -OH groups which is proposed as the rate-limiting step [7]. Klitgaard et al. also suggested that base additives suppressed the catalyst deactivation and restored the catalyst activity in benzyl alcohol oxidation by diminishing the free benzoic acid level in the reaction solution [8]. Zhu et al. identified that the role of base was to provide OH⁻ anions to form Au-OH⁻ sites for the H-abstraction step, which was difficult by using only gold as the active sites [9]. Nevertheless, adding alkaline agents (either tuning the pH in reaction solution or adding promoters to the catalyst) brings several drawbacks: the metal catalyst may dissolve at high pH and be leached out [6]; the base promoter is also susceptible to leaching during the reaction and side reactions could be provoked, *e.g.*, keto-enol equilibration, Cannizzaro reaction, and oxidative decarbonylation [10].

Nowadays, chemical functionalization of catalyst support using a base modifier via the post-synthesis grafting method has been employed as a promising alternative to the addition of alkaline metal hydroxide and cations. Many silane modifiers can be selected to functionalize the support surface to obtain the “customized” surface properties. In addition, these immobilized organic functional groups, such as thiol and amino groups, act as anchoring sites to facilitate the stabilization of metal nanoparticles which are mobile and prone to sinter on the support surface [11]. Development of surface-functionalized catalysts for selective alcohol oxidation has been reported [12]. The localized basicity on the support surface is able to accelerate the alcohol dehydrogenation, suppress side reactions, and enhance the desorption of products without significantly elevating the solution pH [13]. Hu et al. successfully confined highly dispersed Au nanoparticles on the surface of functionalized silica materials, showing a 100% conversion in the benzyl alcohol oxidation [14].

As discussed in Chapter 4, both highly dispersed Au monometallic and Au-Pd bimetallic nanoparticles confined in surface-functionalized SBA-16 are good catalytic materials for the selective oxidation of benzyl alcohol. Nevertheless, limited enhancement of catalytic activity was found and attributed to the mass-transfer restriction. A recent addition to the mesoporous material family is the so-called TUD-1 mesoporous silica [15]. In the synthesis of TUD-1, surfactant and/or block co-polymer are replaced by inexpensive triethanolamine molecules as the structure directing agent. Interestingly, the unique open 3-D sponge-like wide mesoporous structure of TUD-1 can effectively decrease the pore diffusion resistance as we previously demonstrated [16]. In this chapter, we synthesize and characterize a series of Pd catalysts supported on TUD-1 mesoporous silicas functionalized with several organic functional groups, especially amino groups. Afterward, the aerobic oxidation of benzyl alcohol in the absence of any inorganic base is employed as a model reaction to evaluate these as-synthesized Pd catalysts (see Scheme 5.1). The catalytic activity will be benchmarked against Pd catalysts supported on other mesoporous silicas, *e.g.*, MCM-41, SBA-15, and SBA-16. The correlation between catalyst structure, surface chemistry, metal loading, and catalytic activity will be explored and discussed in detail.

Scheme 5.1 Preparation procedures and catalytic evaluation of surface-functionalized TUD-1 supported Pd catalysts.

5.1 Effect of functional groups

The bulk average information of TUD-1 mesoporous silica and the effect of surface-functionalization with various organosilanes were assessed by N_2 physisorption. The amount of different organosilanes was kept as 1.2 mmol/g TUD-1. The nitrogen adsorption-desorption isotherms and the corresponding pore size distributions are illustrated in Figure 5.1. The plots are typical type IV isotherms with a pronounced H3 hysteresis loop characteristic for mesostructured feature with a large pore diameter. Siliceous TUD-1 shows a sharp step increase at $P/P_0=0.6-0.8$ due to the capillary condensation of N_2 inside the mesopores. The step increase shifts to lower P/P_0 , particularly for ATMS-TUD, suggesting a smaller pore size after surface-functionalization with organosilanes, which can be directly observed from the pore size distributions in Figure 5.1b.

Figure 5.1 (a) N₂ physisorption isotherms and (b) pore size distribution of pristine and surface-functionalized TUD-1.

A summary of surface area, pore volume and pore diameter is listed in Table 5.1. Pristine TUD-1 exhibits a BET surface area of $529 \text{ m}^2 \text{ g}^{-1}$, pore volume of $0.99 \text{ cm}^3 \text{ g}^{-1}$, and a narrow pore size distribution centered at 7.5 nm, which are in good agreement with the previous report [16]. Surface-functionalization results in an apparent decrease of these textural parameters, which can be attributed to the immobilization of organic functional groups on the inner wall of mesopores. It is worth mentioning that APS-TUD exhibits a decrease of 0.7 nm in pore diameter. Considering the organic group dimension (ca. 0.6 nm) and assuming these groups adopt a folded conformation [17], this diameter decrease can be suggested as a monolayer of aminopropyl groups covering the inner wall of mesopores. ATMS possesses diamine groups with the longest chain, resulting in a more extended conformation structure; ATMS-TUD shows the most significant variation in pore volume and pore diameter, which is consistent with the lowest onset condensation

step in the N₂ physisorption isotherms. As mentioned above, the average pH of support surface, which reflects the surface chemistry to certain extent, plays a crucial role in the selective oxidation of benzyl alcohol. The results of pH measurement of pristine and surface-modified TUD-1 supports are also summarized in Table 5.1. It is noteworthy that the pH varies significantly with surface-functionalization. The surface of pristine TUD-1 is mildly acidic, showing a pH of 6.3. Surface-functionalization with both APS and ATMS increases the pH to 9.1 and 9.7, respectively, showing that silylation with amino groups provides the effective raise in the surface basicity of silica support. HMDS-functionalization exhibits a neutral surface as expected. Silylation with MPTMS notably reduces the pH to 4.8 due to the presence of thiol group. All these changes in pH validate the successful surface-functionalization and the effectively tuned surface basicity of TUD-1 support.

Table 5.1 Textural properties of pristine and surface-functionalized TUD-1 supports.

entry	Sample	pH	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore diameter (nm)
1	TUD-1	6.3	529	0.99	7.5
2	APS-TUD	9.1	420	0.79	6.8
3	ATMS-TUD	9.7	396	0.62	4.7
4	HMDS-TUD	7.4	403	0.74	6.3
5	MPTMS-TUD	4.8	394	0.72	6.0

Figure 5.2 displays the FTIR spectra of pristine and surface-functionalized TUD-1. All TUD-1 samples, regardless of surface-functionalization, show typical bands at 1090 and 798 cm⁻¹ in the skeletal region of framework vibrations, which are assigned to the asymmetric and symmetric stretching vibrations of Si-O-Si bridges, respectively [18]. The absorbance at 1090 cm⁻¹ has a slight blue shift after surface-functionalization, which can be attributed to the shrinkage of pore structure

[19]. The absorbance at 965 cm^{-1} for pristine TUD-1 assignable to the stretching vibrations of terminal silanol (Si-OH) groups disappears upon the surface-modification [18], implying the successful replacement of terminal silanol groups with organosilane modifiers. Luan et al. suggested that these abundant silanol groups on the inner surface of mesopores serve as the sites for grafting functional groups during the surface-modification [20]. In the hydroxyl region, the weak band at 1633 cm^{-1} and the broad band at 3450 cm^{-1} can be attributed to a combination of the stretching vibration of silanol groups or silanol “nests” with cross hydrogen-bonding interactions and the H-O-H stretching mode of physisorbed water [20]. The absence of these two bands for HMDS-TUD suggests the successful silylation of isolated silanol groups with HMDS, leading to the formation of a hydrophobic surface due to $\text{Si}(\text{CH}_3)_3$ groups. The presence of a broad inconspicuous band at 2960 cm^{-1} , which is characteristic of the asymmetric vibration of the CH_2 groups of silylating agents, further confirms the successful silylation [21].

Figure 5.2 FTIR spectra of pristine and surface-functionalized TUD-1 with different modifiers.

XRD and TEM characterization techniques were introduced to examine the Pd catalysts supported on these surface-functionalized TUD-1 silicas. No distinct diffraction peak can be observed in the XRD patterns for 1 wt.% Pd containing catalysts (Figure 5.3), implying the highly dispersed nature of these metallic nanoparticles. However, for 1Pd/HMDS-TUD, a discernable diffraction peak indexed to the (111) facet of face-centered cubic (FCC) lattice structure of Pd metal suggests a relatively larger particle size for this sample. These XRD analyses can be further confirmed by the direct TEM microscopic observation. The TEM images and the corresponding particle size distributions derived from counting ca. 300 particles are illustrated in Figure 5.4. TUD-1 shows a sponge-like porous structure, suggesting the successful synthesis of TUD-1 mesostructure and good stability after metal adsorption and reduction. In agreement with nitrogen physisorption results, the lack of long-range ordered mesostructure in TUD-1 after metal adsorption and reduction is also reflected in the TEM image. 1Pd/TUD exhibits a broad palladium particle size distribution centered at 7.0 nm, which is consistent with the pore diameter of pristine TUD-1 (7.5 nm), implying the encapsulation of Pd nanoparticles in the mesopores of TUD-1. Upon surface-functionalization, 1Pd/APS-TUD, 1Pd/ATMS-TUD and 1Pd/MPTMS-TUD show narrow particle size distributions with mean size of 1.9, 3.2 and 1.6 nm, respectively. Nonetheless, 1Pd/HMDS-TUD exhibits a considerably wide particle size distribution with a mean particle size of 17.0 nm.

After surface-functionalization via the silylation of TUD-1 silica matrix with various organosilanes, these immobilized functional groups bonded onto the inner pore wall surface of TUD-1 act as anchors for the metal adsorption. Hydrophilic amino groups (-NH₂) and thiol groups (-SH) show great affinity to the aqueous

palladium chloride and therefore facilitate the deposition of metal precursor and the formation of small and highly dispersed Pd nanoparticles embedded on TUD-1. Furthermore, 1Pd/HMDS-TUD with hydrophobic trimethyl groups shows a barrier for the adsorption of Pd precursor and leads to the formation of large Pd particles with broad particle diameter distribution. 1Pd/APS-TUD displays a narrower Pd particle size distribution and a smaller mean particle diameter than 1Pd/ATMS-TUD (see Figure 5.4b and c). Lee et al. also reported a similar result and they attributed it to the strong interaction between Pd nanoparticles and the grafted diamino groups [22]. The substantially small pore diameter and pore volume of 1Pd/ATMS-TUD may also play a role in forming the Pd nanoparticles with an irregular size distribution, which was indicated in our previous report [23].

Figure 5.3 XRD patterns of 1Pd/TUD surface-functionalized with different modifiers.

Figure 5.4 TEM micrographs and particles size distributions of (a) 1Pd/TUD; (b) 1Pd/1.2APS-TUD; (b) 1Pd/ATMS-TUD; (d) 1Pd/HMDS-TUD; (e) 1Pd/MPTMS-TUD.

We introduced the solvent-free selective oxidation of benzyl alcohol using molecular oxygen as a model reaction to examine these as-synthesized Pd catalysts, aiming to elucidate the effect of surface-functionalization on catalytic performance. The catalytic results of these Pd catalysts are listed in Table 5.2 where q_{TOF} was determined by using the Pd content obtained from ICP and subtracting the non-catalytic effect (conversion ~5%). During the reaction, benzaldehyde is produced as the main product along with a trace amount of toluene and benzoic acid as byproducts. The catalytic activity is remarkably enhanced upon the surface-functionalization after we rule out the effect of actual metal loadings. Among all the catalysts, 1Pd/MPTMS-TUD shows the best catalytic activity with a conversion of 26.3% and an exceptionally high q_{TOF} of 29 456 h⁻¹, which is twice that of 1Pd/TUD. Nevertheless, this high activity is accompanied by the formation of a large amount of toluene and benzoic acid, resulting in consequently low benzaldehyde selectivity (81.5%). No toluene was detected for other surface-modified catalysts and benzoic acid is the only byproduct.

Table 5.2 Catalytic properties of Pd containing catalysts supported on pristine and surface-functionalized TUD-1^a.

Catalyst	Pd content ^b (wt.%)	Conversion (%)	Selectivity (%)			q_{TOF}^c (h ⁻¹)
			benzaldehyde	toluene	benzoic acid	
1Pd/TUD	0.68	13.2	91.7	1.5	6.8	12910
1Pd/APS-TUD	0.99	22.3	95.2	0	4.8	18571
1Pd/ATMS-TUD	0.97	17.0	93.5	0	6.5	13179
1Pd/HMDS-TUD	0.41	11.5	91.5	0	8.5	16802
1Pd/MPTMS-TUD	0.77	26.3	81.5	17.7	0.8	29456

^a Reaction conditions: benzyl alcohol/Pd = 250 mol/g; O₂, 20 mL min⁻¹; temperature, 433 K; time, 1h.

^b Pd content was tested by ICP.

^c q_{TOF} is calculated by using the Pd content obtained from ICP and subtracting the non-catalytic effect (conversion ~5%).

Recalling the TEM results in Figure 5.4, uniform Pd nanoparticles with a narrow size distribution centered at 1.6 nm on 1Pd/MPTMS-TUD explain the remarkably high activity of this particular catalyst, implying that the Pd nanoparticle size plays a vital role in controlling the catalytic activity, which is coincident with the results reported by Li et al. [4]. Nevertheless, the catalytic activity of noble metal catalysts in the selective oxidation of alcohols heavily relies on the metal-support interaction in addition to the mean metal particle size. Over 1Pd/MPTMS-TUD, a large amount of toluene as byproduct is induced by the acidic surface due to the hydrolysis of –SH groups, as suggested by Enache et al. [24]. Furthermore, the generation of benzoic acid is suppressed, and thus the improvement of benzyl alcohol conversion over 1Pd/MPTMS-TUD is mainly attributed to the formation of toluene by disproportionation of benzyl alcohols. The extremely low Pd content in 1Pd/HMDS-TUD is due to the adsorption barrier of aqueous palladium precursor onto the hydrophobic surface in the presence of trimethyl groups. This particular catalyst exhibits the lowest benzyl alcohol conversion (11.5%), which probably resulted from the lack of active sites due to the extremely low Pd content as well as the large and irregular Pd nanoparticles as indicated in XRD and TEM.

For amino group-functionalized catalysts, *i.e.*, both 1Pd/APS-TUD and 1Pd/ATMS-TUD, the surface is basic due to the hydrolysis of amino groups, which slightly promotes the formation of benzoic acid. The elevated surface basicity is suggested to enhance the dehydrogenation of benzyl alcohol which is the rate-controlling step during the reaction, suppress the formation of byproduct toluene, as well as facilitate the reactant adsorption and product desorption from the Pd active sites. Although APS and ATMS both contain amino groups, 1Pd/APS-TUD exhibits larger enhancement in the catalytic activity as well as the

selectivity. This is mainly due to the formation of larger Pd nanoparticles with fewer active sites for the reaction in 1Pd/ATMS-TUD as suggested by TEM because diamine groups in ATMS show stronger interaction with Pd nanoparticles than that of monoamine groups in APS. After considering both excellent catalytic activity and high selectivity towards benzaldehyde, APS was selected as the best modifier in the following study.

5.2 Effect of APS amount

The nitrogen physisorption patterns of TUD-1 surface-functionalized with different APS contents varying from 0.3 to 3.6 mmol/g TUD-1, as shown in Figure 5.5, exhibit irreversible type IV isotherms which are identical to that of pristine TUD-1. Increasing the APS loading amount notably shifts the hysteresis towards a lower relative pressure (P/P_0) and slightly decreases the overall nitrogen adsorption volume, implying the successful grafting of APS on the inner wall of TUD-1 mesopores. The narrow pore size distributions are also shown in Figure 5.5b.

Figure 5.5 (a) N_2 physisorption isotherms and (b) pore size distribution of TUD-1 surface-functionalized with different APS contents.

The calculated textural parameters of TUD-1 modified with various APS amounts are listed in Table 5.3. The APS-modified TUD-1 samples show comparable structural parameters to the parent TUD-1, implying that the integrity of pristine mesoporous structure is retained after the surface-grafting procedure. A trend of decreasing surface area, pore volume, and pore diameter with increasing the APS content can be observed, which is attributed to the self-assembly and incorporation of functional groups into the framework of mesoporous materials. The results of pH measurement of TUD-1 supports surface-functionalized with different APS amounts are also listed in Table 5.3. Increasing the APS amount notably increases the pH level from 6.3 for pristine TUD-1 to 9.1 for 1.2APS-TUD, indicating that the local surface basicity can be remarkably elevated after silylation with an appropriate amount of APS. However, further increasing the APS content does not substantially increase the pH value, which is probably due to that a maximum grafting amount of APS exists as suggested by Ramila et al. [25].

Table 5.3 Textural properties of APS-functionalized TUD-1.

Entry	Sample	pH	Surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	Pore diameter (nm)
1	TUD-1	6.3	529	0.99	7.5
2	0.3APS-TUD	7.8	515	0.99	6.8
3	0.6APS-TUD	8.2	502	0.88	6.3
4	1.2APS-TUD	9.1	420	0.79	6.8
5	2.4APS-TUD	9.1	416	0.76	5.9
6	3.6APS-TUD	9.2	362	0.64	5.5

According to Xu et al., well-isolated amino group and hydroxyl group absorption bands cannot be resolved using FTIR because of the bending vibration overlap between N-H and hydroxyl or silanol groups in IR range [26]. Near-infrared (NIR) is superior to IR for characterizing amino groups because amino groups exhibit well-resolved absorption bands in the NIR region (1000 to 2500 nm). As illustrated in Figure 5.6.

Figure 5.6 The UV-vis-NIR spectra of pristine and APS-functionalized TUD-1 with different APS contents.

All the APS modified TUD-1 samples display two major absorption bands: 1897 nm assignable to the combination of stretching and deformation vibrations for adsorbed water and 1403 nm ascribable to the first overtone of the stretching frequencies of silanol groups and adsorbed water [27]. Upon grafting APS onto TUD-1 surface, the reflection bands at 1528 and 2020 nm appear and become more and more intense as increasing the APS loading amount. These two bands are indexed to the combination band of asymmetry stretching (ν_{asym}) and symmetry stretching (ν_{sym}) modes and the combination band of stretching vibration (ν) and bending (δ) modes of the amino groups, respectively [28]. Moreover, the reflection bands between 1600 and 860 nm are assigned to the stretching vibration of CH_2 moiety in the propyl chain of the APS silane modifier [29]. The UV-vis-NIR spectra provide further evidence that after surface-modification with APS, the amino functional groups are indeed grafted onto the silica surface and covalently bonded to the inner wall of mesopores.

Vibrational spectroscopy techniques, *e.g.*, IRAS, have been regarded as exceptionally useful tools for elucidating the heterogeneous catalytic reaction mechanisms, indentifying the active species on a catalyst surface with sub-monolayer accuracy, and addressing the particle size and morphology effects and particle-support interactions. In this chapter, IRAS was employed using CO as a probe molecule to identify specific interaction between Pd nanoparticles and amino groups. All samples show the characteristic features for CO adsorption on Pd nanoparticles, see Figure 5.7. The bands at 2172 and 2114 cm^{-1} are assigned to the absorption of residual gaseous CO, which do not change with increasing the APS amount. The C-O stretching bands at around 2057 and 1873 cm^{-1} correspond to the CO molecules adsorbed on top and threefold hollow sites on a (111) facet of Pd nanoclusters respectively, suggesting that TUD-1 supported Pd nanoparticles in this study exhibit predominantly (111) facets, which in agreement with previous reports [30].

With increasing grafted amount of aminopropyl groups, the absorption band at 2057 cm^{-1} becomes boarder and slightly blue shifts to high wave number. In particular, this band shifts to 2069 cm^{-1} and becomes an imperceptible shoulder for 1Pd/1.2APS-TUD. When the APS contents further increase, this band becomes narrower and shifts back to 2057 cm^{-1} as that of Pd supported on pristine TUD-1. The information of Pd nanoparticle size and interaction between Pd and amino groups can be indirectly derived from this variation of absorption bands. The decreased Pd nanoparticle size can lead to the broadening and blue shift of CO stretching band in IRA spectra, which is due to the increased number of defect sites (such as edges and kinks) and disorder on a small Pd nanoparticle, as suggested by Ozensoy and Goodman [30]. Hollins reported that the increase in CO stretching

frequency is also attributed to a weaker CO-metal interaction, resulting in a reduced occupation of CO 2π orbital when CO is bound at a high-coordinated metal atom [31]. With increased the grafting content of aminopropyl groups, Pd atoms have higher coordination with the surrounding amino groups; the interaction between Pd nanoparticles and the APS-modified TUD-1 becomes stronger. Hence, the interaction between Pd and adsorbed CO gets weaker and less CO 2π orbit is occupied, leading to the blue shift of the CO stretching band.

Figure 5.7 IRA spectra for CO adsorption on 1Pd/APS-TUD with different APS contents. CO dosage and measurement performed at room temperature.

To further investigate the structural and electronic properties of these Pd nanoclusters, Pd $3d$ XPS measurements were conducted and the results of four selected 1Pd/APS-TUD samples are illustrated in Figure 5.8. All the samples show a typical doublet of $3d$ core level bands centered around 340 and 335 eV, which are assigned to $\text{Pd}^0 3d_{3/2}$ and $\text{Pd}^0 3d_{5/2}$, respectively [32]. Recently, Radkevich *et al.* have demonstrated the amino groups possessing electron-donor properties can increase the proportion of Pd^0 and the resistance against re-oxidation of Pd^0 due to

the electronic interactions between nitrogen atoms and Pd metallic nanoparticles, which are active centers for hydrogenation-dehydrogenation reactions [33]. We cannot draw the same conclusion because no oxide peak is detected throughout the whole Pd 3d region, implying the formation of Pd metallic nanoparticles by completely reducing the palladium precursors. With increasing grafted amount of APS, both bands undergo a negative shift to lower binding energies. The maximum shift (1 eV) as compared to the binding energy of Pd supported on pristine TUD-1 can be observed on 1Pd/1.2APS-TUD. With further increase in the APS content, both bands exhibit a shift back to high binding energy. Fox *et al.* suggested that the shift to low binding energy indicates the high dispersion of Pd species [34]. It is worthwhile noticing that this trend of binding energy shift is identical to that of CO adsorption peak from IRAS and can be understood as complementary evidence of the APS amount effect on the interaction between Pd nanoparticles and amino groups.

Figure 5.8 Pd 3d XPS spectra of 1Pd/APS-TUD catalysts with various APS contents.

The XRD patterns of 1Pd/APS-TUD catalysts with different APS amounts are shown in Figure 5.9. There is no obvious discrepancy in Pd nanoparticles dispersion among all the 1Pd/APS-TUD catalysts because no noticeable diffraction peak can be observed in the XRD patterns.

Figure 5.9 XRD patterns of TUD-1 surface-functionalized with different APS contents.

The TEM images are shown in Figure 5.10. The mean Pd particle size is reduced from 7.0 to 5.8 nm upon increasing surface-modification with APS. It decreases to 1.9 nm with a narrow size distribution for 1Pd/1.2APS-TUD. Nevertheless, larger Pd nanoclusters are generated with a boarder particle size distribution for 1Pd/3.6APS-TUD due to the excess amount of APS. This trend is consistent with IRAS and XPS results. It can be verified that the grafting amount of amino groups plays an important role in controlling the size and morphology of Pd nanoparticles, *i.e.*, small and homogeneous Pd nanoparticles formed upon surface-functionalized with APS, whereas further loading excess APS results in

large and irregular nanoparticles. A specific interaction between Pd nanoclusters and APS immobilized TUD-1 support is also evidenced.

Romanmartinez *et al.* suggested that the distribution of metal precursors on the support and the specific metal-support interaction are strongly dependent on the support surface chemistry [35]. This APS effect on the size control of Pd nanoparticles can be explained by the nature of the support surface which results in different interactions between metal and support. Due to the hydrolysis in the metal adsorption procedure, the silica surface without APS group is mildly acidic and negatively charged, which hinders the diffusion and adsorption of negatively charged $\text{PdCl}_2(\text{OH})_2^{2-}$ species. After substituting the terminal silanol groups with amino groups, the surface is positively charged due to the hydrolysis of $-\text{NH}_2$ groups, exhibiting great affinity to the palladium precursors, thus the palladium precursors can be easily adsorbed into the mesopores. In addition, these immobilized amino groups are suggested to act as anchors to stabilize the Pd nanoparticles by binding them through covalent interactions, resulting in highly dispersed and uniformly distributed Pd nanoparticles [11]. Nevertheless, further adding APS may result in the oligomerization and polymerization of organosilanes into the form of a cross-linked monolayer of alkanolamine attached on the surface; partially blocking the mesopores occurs as suggested in nitrogen physisorption (see Table 5.3) [36]. More Pd nanoparticles on the external surface of the support are susceptible to agglomeration due to the lack of structural confinement [23]. Thus, there is a optimized amount of APS functional groups to substitute the silanol groups and occupy the pore volume, which was also demonstrated by other groups [20, 25]. In this study, the effect of APS content is pronounced between 1.2APS-TUD substrate and Pd species.

Figure 5.10 TEM micrographs and particles size distributions of 1 Pd/APS-TUD with different APS contents: (a) 1Pd/0.3APS-TUD; (b) 1Pd/0.6APS-TUD; (c) 1Pd/1.2APS-TUD; (d) 1Pd/2.4APS-TUD; (e) 1Pd/3.6APS-TUD.

To examine the effect of grafted APS content on the catalytic activity, benzyl alcohol oxidation over 1Pd/APS-TUD catalysts with different APS amounts was investigated and illustrated in Figure 5.11. The catalytic activity is improved when APS is grafted. 1Pd/1.2APS-TUD shows the highest conversion and selectivity towards benzaldehyde of 22.3% and 95.2%, respectively. Further increasing the APS loading slightly decreases the catalytic activity and selectivity. The trend of benzyl alcohol conversion implies the activity of supported Pd catalysts is mainly dependent on the particle size and size distribution [4] as well as the local surface basicity. The outstanding catalytic behavior of 1Pd/1.2APS-TUD resulted from the small and uniform Pd nanoparticles due to the enhanced metal-support interaction and the appropriate surface basicity. 1Pd/1.2APS-TUD was selected as the optimal catalyst in the following work.

Figure 5.11 Catalytic performance of 1Pd/APS-TUD catalysts with different APS contents. Reaction conditions: benzyl alcohol/Pd = 250 mol/g; O₂, 20 mL min⁻¹; temperature, 433 K; reaction time, 1h.

5.3 Effect of Pd loading

The XRD patterns of Pd/1.2APS-TUD with different Pd loadings (0.5-3 wt.%) illustrate that only 3Pd/1.2APS-TUD shows a weak and broad diffraction peak assigned to the (111) facet of FCC lattice structure for Pd nanoparticles, suggesting the formation of large and irregular Pd nanoclusters in this particular sample. It is further demonstrated by the direct TEM microscopic images as displayed in Figure 5.12. Increasing Pd loading results in a larger mean particle diameter, varied between 1.3 nm for 0.5Pd/1.2APS-TUD and 6.5 nm for 3Pd/1.2APS-TUD. Moreover, the nanoparticles on 3Pd/1.2APS-TUD show a wide size distribution. This discrepancy is mainly caused by the agglomeration of Pd nanoparticles due to high Pd content.

Figure 5.12 TEM micrographs and particles size distributions of Pd/1.2APS-TUD with various Pd loading: (a) 0.5Pd/1.2APS-TUD; (b) 1Pd/1.2APS-TUD; (c) 2Pd/1.2APS-TUD; (d) 3Pd/1.2APS-TUD.

The catalytic results of benzyl alcohol oxidation over Pd/1.2APS-TUD catalysts with different Pd loadings are shown in Figure 5.13. All catalysts exhibit a high and constant selectivity around 96% towards benzaldehyde. The benzyl alcohol conversion increases as the Pd loading rises from 0.5 to 1 wt.%, which is due to the

increased number of active sites available participating in the reaction. The conversion slightly decreases upon further adding Pd, which can be attributed to the agglomeration of nanoparticles which decreases the available number of active sites for the reaction at a high Pd content [4]. Among all the samples, 1Pd/1.2APS-TUD shows the best catalytic result with a remarkably high q_{TOF} of 18571 h^{-1} and is regarded as the best catalyst in this study.

Figure 5.13 Catalytic performance of Pd/1.2APS-TUD with various Pd loadings and inset table of activation energy. Reaction conditions: benzyl alcohol/Pd = 250 mol/g; O_2 , 20 mL min^{-1} ; temperature, 433 K; time, 1 h.

The inset table in Figure 5.13 lists the activation energy (E_a) of these catalysts in aerobic oxidation of benzyl alcohol determined from the Arrhenius plots. These activation energy values are comparable to that of TiO_2 supported noble metal catalysts reported by Enache *et al.* (45.8 kJ/mol) [24], and much higher than the Pd catalyst supported on SBA-16 (12.3 kJ/mol) [37]. It was reported that low activation energy in a liquid phase reaction indicates the alcohol oxidation is likely to be mass-diffusion limited and controlled by the access of reactants to active sites [38].

This suggests that the unique 3-D sponge-like mesoporous structure of TUD-1 can effectively eliminate the diffusion limitation.

5.4 Study of 1Pd/1.2APS-TUD

The 1Pd/1.2APS-TUD catalyst, which has been verified to provide best performance for the solvent-free oxidation of benzyl alcohol, was investigated in detail. The time course of 1Pd/1.2APS-TUD for benzyl alcohol oxidation was monitored periodically, as depicted in Figure 5.14.

Figure 5.14 Time course of 1Pd/1.2APS-TUD for benzyl alcohol oxidation.

Reaction conditions: benzyl alcohol/Pd = 250 mol/g; O₂, 20 mL min⁻¹; temperature, 433 K.

The conversion of benzyl alcohol increases monotonically with the reaction time on line, while *q*TOF declines. Interesting, the selectivity toward benzaldehyde is rather low (81.5%) at first 0.5 h of reaction, sharply rises to 95.2% at 1 h, and gradually drops again with further reaction time. The low selectivity at 0.5h is attributed to the formation of large amount of toluene (15.8%), which is produced from the hydrogenolysis of benzyl alcohol facilitated by hydrogen adsorbed on Pd

surface formed in the dehydrogenation step at the beginning of reaction [39]. The decay of selectivity at long reaction time is probably ascribed to the generation of benzoic acid due to the further oxidation of benzaldehyde.

From the point of potential practical application in the future, the effect of reaction conditions (temperature, oxygen flow rate) for benzyl alcohol oxidation is examined and summarized in Table 5.4. Neither TUD-1 nor surface-functionalized TUD-1 displays catalytic activity for benzyl alcohol oxidation at low temperature, excluding the effect of support. The selectivity toward benzaldehyde is well maintained above 95% when the temperature varied from 80 to 160 °C (Entry 1-5). However, the benzyl alcohol conversion is negligible at low reaction temperature, but increases remarkably when the temperature is elevated from 120 to 160 °C. It is noteworthy that the benzyl alcohol conversion displays particularly a 10-fold enhancement from 100 to 160 °C. This trend is consistent with the activation energy listed in Figure 5.11. The high E_a indicates the absence of mass-transport limitation, as well as the large energy barrier for the reaction. Therefore, high temperature is required to provide a large amount of energy to initiate the reaction. The O_2 flow also has impact on the catalytic performance. The selectivity to benzaldehyde is low accompanied by formation of a large amount of toluene at low O_2 flow rate, and gradually improved with the elevated flow rate (Entry 5-7).

Toluene has been verified to be the major byproduct under anaerobic condition due to the deficiency of surface oxygen which therefore results in either a concentrated nucleophilic attack of a surface hydride to the benzylic carbon of adsorbed benzyl alcohol or the recombination of $[PhCH_2(ad)]$ with $[H(ad)]$ [40]. Moreover, the slight decay of conversion at low O_2 flow rate also implies the

possible existence of external diffusion effect, which can be eliminated by increasing the O₂ flow rate.

Table 5.4 Effect of reaction conditions for 1Pd/1.2APS-TUD on alcohol oxidation^a.

Entry	Substrate	T (°C)	O ₂ flow rate (mL min ⁻¹)	Conversion (%)	Selectivity ^b (%)	qTOF (h ⁻¹)
1	benzyl alcohol	80	20	0.8	96.2	908
2	benzyl alcohol	100	20	2.2	96.6	2316
3	benzyl alcohol	120	20	3.0	96.2	3251
4	benzyl alcohol	140	20	10.7	94.5	11493
5	benzyl alcohol	160	20	22.3	95.2	18571
6	benzyl alcohol	160	10	18.8	83.7	14847
7	benzyl alcohol	160	5	14.4	79.9	13329
8	1-phenylethanol	160	20	27.5	98.2	29576
9	4-methylbenzyl alcohol	160	20	6.0	97.2	6437
10	4-nitrobenzyl alcohol	160	20	1.0	100	1025
11	4-bromobenzyl alcohol	160	20	0.8	100	874
12	cinnamyl alcohol	160	20	14.4	100	15493

^a Reaction conditions: substrate/Pd = 250 mol/g; time, 1h.

^b Selectivity refers to the corresponding aldehyde or ketone; for benzyl alcohol, byproducts are toluene and benzoic acid; for 1-phenylethanol, byproduct is ethylbenzene; for 4-methylbenzyl alcohol, byproduct is *p*-xylene.

To access the scope of this particular Pd/APS-TUD catalyst, a variety of aromatic alcohols were employed to examine the generality of 1Pd/1.2APS-TUD for alcohol oxidation; the results are listed in Table 5.4 (Entry 8-12). The selectivity towards the corresponding aldehyde or ketone is remarkably high for all the alcohols investigated. High conversion (27.5%) was obtained for 1-phenylethanol oxidation, implying the higher reactivity of secondary alcohol compared than primary alcohol. For the oxidation of 4-methylbenzyl alcohol, the conversion is poor but non-ignorable. However, little activity can be observed for the oxidation of

4-nitrobenzyl alcohol and 4-bromobenzyl alcohol, suggesting this 1Pd/1.2APS-TUD catalyst shows higher catalytic activity for substituted aromatic alcohols containing electron-donating group (*e.g.* -CH₃) than those containing electro-withdrawing groups (such as -NO₂ and -Br), which is consistent with the results reported previously [41]. Additionally, this catalyst also displays a noticeable conversion for the oxidation of cinnamyl alcohol (Entry 12), suggesting the effective catalytic activity for oxidizing allylic alcohols.

The recyclability has been taken as a curial factor in evaluating a heterogeneous catalyst participating in a multi-phase system. The metallic components with weak stability and poor recyclability can leach out during the course of reaction, resulting in the formation of an active homogeneous catalyst and a loss of catalytic activity on subsequent consecutive runs. The recyclability of 1Pd/1.2APS-TUD catalyst in the solvent-free selective oxidation of benzyl alcohol with molecular oxygen was examined. The catalyst was recovered after each reaction run, washed with acetone, dried at 333 K, and reused in a new reaction. Figure 5.15 shows the recyclability of 1Pd/1.2APS-TUD for 5 consecutive cycles. The catalytic activity and selectivity only undergo a moderate decrease, which is attributed to the loss of catalyst during recovery. The Pd content after 5 consecutive reaction cycles was almost the same as that of fresh catalyst and Pd cannot be detected by ICP analysis in the filtrate after the reaction. Moreover, no noticeable conversion of benzyl alcohol was observed when the liquid filtrate was employed instead of the solid catalyst for further reaction, further confirming that there was no leaching of Pd and this 1Pd/1.2APS-TUD catalyst can be fully recycled. Therefore, APS-modified TUD-1 supported Pd catalysts not only dramatically improve the

catalytic performance but also show superiority in enhancing the resistance against deactivation.

Figure 5.15 Recyclability of 1Pd/1.2APS-TUD catalyst for benzyl alcohol

oxidation of with molecular oxygen. Reaction conditions: benzyl alcohol/Pd = 250 mol/g; O₂, 20 mL min⁻¹; temperature, 433 K; time, 1h.

5.5 Discussions

To demonstrate the advantage of TUD-1's unique mesostructure in the liquid phase reaction, we investigated the catalytic performances of Pd catalysts supported on various surface-functionalized mesoporous silica materials, including TUD-1, MCM-41 and SBA-15 with 2-D hexagonal structure and SBA-16 with 3-D cubic cage-like structure. As depicted in Figure 5.16, TUD-1 shows superior catalytic activity relative to other silica materials, regardless of the surface-functionalization. SBA-16 shows a moderate performance, whereas MCM-41 and SBA-15 exhibit a similar but rather low activity. This can be attributed to the effect of different mesoporous structures since the formation of metal nanoparticles is mainly controlled by the architecture of the host material. On MCM-41 and SBA-15, Pd

nanoparticles show a high degree of thermal sintering within the straight mesochannels, leading to the migration and coalescence of Pd nanoparticles and thereby the ineffective catalytic performance. The inferior performance of SBA-15 as compared to MCM-41 is due to the interconnected micropores in SBA-15 where Pd nanoparticles may be completely buried and inactive. Although the “super-cage” porosity of SBA-16 is superior for confining metal nanoparticles with high dispersion in a “ship-in-a-bottle” way, which has been previously proven by our group [23, 37], the mass-diffusion limitation is severe and its inferior catalytic activity is due to the restriction by the diffusion of reactants to active sites during the reaction.

Figure 5.16 Catalytic performance of Pd catalysts supported on pristine and surface-functionalized mesoporous silica supports. Reaction conditions: benzyl alcohol/Pd = 250 mol/g; O₂, 20 mL min⁻¹; temperature, 433 K; time, 1h.

For TUD-1, the mesopores have larger diameter than that of SBA-16 and are randomly interconnected. The tortuous pore arrangements can help to provide sufficient defects to encapsulate and restrict the mobility of nanoparticles that lead to thermal sintering and growth of particles, and prevent the active centers from reactant poisoning. In addition, according to our previous report, TUD-1 with open 3-D mesopore structure and large pore size can effectively decrease the pore diffusion resistance of the reactants. Therefore, it can provide greater access of the reactants to the active sites embedded on the pore wall surface [16]. The excellent catalytic performance of TUD-1 supported Pd catalysts herein again verifies the superiority of the 3-D sponge-like mesostructure of TUD-1. Hence, upon the APS-modification, palladium precursors can be easily adsorbed and Pd nanoparticles are uniformly embedded in the mesopores of TUD-1 with a specific size distribution. The suppressed mass-transfer limitation, enhanced metal-support interaction, and a finely tuned local basicity surrounding the Pd nanoparticles result in a remarkably improved catalytic performance.

It is clear that local surface basicity and Pd nanoparticle size are two vital factors controlling both the catalytic activity (q_{TOF}) and selectivity. Nevertheless, the surface basicity also affects the particle size and size distribution as well as the dehydrogenation step in the benzyl alcohol oxidation, resulting in the complex and ambiguous explanation of the effect of individual factors and their interaction on the catalytic performance. To facilitate more rigorous interpretation, we employed statistical techniques to develop a second-order polynomial regression model including both linear and quadratic terms to fit the experimental data of two factors (x_1 : Pd size, x_2 : pH value) and two responses (y_1 : q_{TOF} , y_2 : selectivity).

Prior to model development, factors are normalized to the range of [-1, 1] to improve numerical accuracy, which is a standard procedure [42]. The experimental data are fit by two multiple linear regression (MLR) models, one for relating q TOF (y_1) and the other for selectivity (y_2). Preliminary inspection on the data clearly indicates that neither y_1 nor y_2 is a linear function of the factors, and thus second-order MLR is developed by including quadratic and cross terms of the two factors (x_1 : Pd size; x_2 : pH value). The estimated model parameters are given in Table 5.5. The model for q TOF provides exceptionally good fit to the data according to the adjusted R^2 value being close to unity, while the model for selectivity has a lower yet still satisfactory accuracy ($R_{adj}^2=0.85$). Further, we suspect that some regression terms may not have significant influence on the response. The statistically significant terms may be identified by using a stepwise selection/elimination procedure [42-43] with the objective of minimizing the well-known Akaike's information criterion (AIC). The stepwise method does not remove any term from the q TOF model, confirming that all the terms are significant for predicting q TOF. In contrast, this procedure removes x_2 and x_2^2 from the selectivity model (last column of Table 1) and results in improved model accuracy ($R_{adj}^2=0.88$).

Table 5.5 The parameter estimates of the MLR models for q TOF and selectivity.

Term	Model for q TOF ($R_{adj}^2>0.99$)	Model for selectivity ($R_{adj}^2=0.85$)	Model for selectivity, after stepwise selection ($R_{adj}^2=0.88$)
Intercept	19753.3	91.10	85.94
x_1	5787.1	-1.11	-2.17
x_2	8196.8	1.10	(removed)
x_1^2	-21677.9	-27.08	-10.55
x_2^2	-43109.2	-16.31	(removed)
x_1x_2	-60288.2	-45.84	-18.22

The contour plots of q TOF and selectivity provide a rational examination of the influence of each experimental variable on the responses, as illustrated in Figure 5.17. Both contour plots are elliptically shaped, implying the significant interaction between pH and Pd size [43]. It is obvious that to obtain high q TOF at small Pd size, the catalyst surface has to be mildly alkaline. Similarly, high selectivity can be achieved at small Pd size and high pH level, and vice versa. Both contour plots reflect similar trend and therefore the adjustment of Pd size and surface basicity will affect the catalytic results remarkably. Based on the normalized variables and the improved model, the prediction formulas of y_1 (q TOF) and y_2 (selectivity) are as follows:

$$y_1 = 19753.3 + 5787.1x_1 + 8196.8x_2 - 21677.9x_1^2 - 43109.2x_2^2 - 60288.2x_1x_2$$

$$y_2 = 85.94 - 2.17x_2 - 10.55x_1^2 - 18.22x_1x_2$$

These quadratic polynomial equations, which were developed to predict the response as a function of the variables and their interactions variables, can be used to determine the catalytic results (q TOF and selectivity) quantitatively and facilitate precise optimization of the reaction parameters.

Figure 5.17 Contour plots of q_{TOF} (top) and selectivity (bottom) as a function of Pd size and pH of support.

5.6 Conclusions

In this chapter, a series of Pd catalysts supported on TUD-1 functionalized with various organosilanes (APS, ATMS, HMDS, and MPTMS) were successfully prepared using a surface-modification scheme followed with a metal adsorption-reduction procedure. The catalytic activities of these as-prepared catalysts were explored in the solvent-free selective oxidation of benzyl alcohol using molecular oxygen. The catalytic results proved that the type and amount of functional group for functionalizing the TUD-1 support showed great impact on the

catalytic performance. APS immobilized on TUD-1 with an appropriate amount of APS coverage displayed the best improvement owing to the enhanced metal-support interaction and finely tuned local surface basicity surrounding the Pd nanoparticles. Among all the catalysts, 1Pd/1.2APS-TUD exhibited a dramatically high q_{TOF} of 18571 h^{-1} for benzyl alcohol conversion. TUD-1 is superior to other mesoporous silicas due to its unique open 3-D sponge-like wide mesostructure which can effectively confine the nanoparticles and suppress the mass-diffusion resistance. This work has been published in Journal of Catalysis (Chen *et al.* Journal of Catalysis, 2010, 275 (1), 11-24); reuse in this chapter is under the permission of Elsevier Global Rights Department.

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Chapter 6 Formation of monometallic Au, Pd and bimetallic Au-Pd nanoparticles confined in mesopores via Ar glow discharge plasma reduction and their catalytic applications in aerobic oxidation of benzyl alcohol

Tremendous efforts have been devoted to developing heterogeneous noble metal catalysts from the viewpoints of atomic efficiency and environmental-benign process. Supported gold (Au) and palladium (Pd) nanoparticle catalysts have been investigated intensively [1-4] since the first successful CO oxidation over Au and the application of Pd in catalyzing aerobic oxidation of alcohols reported by Haruta *et al.* [5] and Blackburn and Schwartz [6], respectively. Bimetallic nanoparticle is of greater interest than monometallic one for improving the catalytic properties due to the synergetic effect between two elements. Recently, several research groups have examined the supported Au-Pd bimetallic catalysts with remarkably enhanced catalytic activity and product selectivity in various alcohol oxidation reactions. Enache *et al.* reported an extraordinarily high TOF ($269\,000\text{ h}^{-1}$) of Au-Pd/TiO₂ in 1-phenylethanol selective oxidation, showing that the combination of gold and palladium in an alloyed nanoparticle configuration led to a 25-fold improvement in the catalytic activity [7]. The advantage of bimetallic catalyst is attributed not only to the electronic interaction between two metals but also to the complex structure of bimetallic nanoparticles. Several studies tested different bimetallic nanoparticle structures, such as core-shell structure [8], cluster-in-cluster structure [9], and single alloy structure [10]. In Chapter 4, we reported the Au-Pd bimetallic nanoparticle with a Pd cluster-on-Au cluster structure confined in the super-cage of SBA-16 mesoporous materials, which exhibited an excellent catalytic activity for benzyl alcohol oxidation [3].

Different preparation procedures may result in variation in the particle size,

morphology, structure and electron property of bimetallic nanoparticle catalysts, which thereby significantly affect the metal-support interaction and consequently the catalytic performance. The pre-treatment step, *e.g.*, reduction is essential to obtain uniform and well dispersed metallic active species. Conventionally, the catalysts are reduced by flowing hydrogen (H_2) at elevated temperatures or by chemical reactants, such as formaldehyde and hydrazine. Nonetheless, H_2 requires special care for production, transportation, storage and use, while most chemical reducing agents currently employed in catalyst preparation are hazardous to both human body and environment. Our group previously reported a facile microwave-assisted polyol reduction (MAPR) method, in which ethylene glycol served as both solvent and reducing agent [4]; nonetheless, high temperature and microwave radiation are required. Recently, a green, rapid, facile and energy efficient glow discharge plasma reduction route has been reported to reduce supported metal catalysts using inert gas (Ar) as the plasma forming gas [11-13]. This novel plasma reduction is operated at ambient temperature, which significantly reduces the energy consumption and cost as well as emission of the toxic and hazardous materials.

Herein, the Ar glow discharge plasma reduction was employed to synthesize monometallic Au, Pd and bimetallic Au-Pd nanoparticles confined in mesochannels of SBA-15 silicas. In view of the importance of alcohol dehydrogenation to ketone and aldehyde which are valuable intermediates/products for the pharmaceuticals, agrochemicals, and perfumery industries [14-16], the solvent-free aerobic oxidation of benzyl alcohol to benzaldehyde is chosen as the model reaction to test the catalytic performances of plasma reduced noble metal nanoparticle catalysts. The effects of plasma treatment on the structure/configuration and catalytic activity of

nanoparticle catalysts were carefully examined and benchmarked against conventional H₂ thermal reduction. Post-treatments (oxidation and re-reduction) were carried out to further reveal the stability of plasma reduced bimetallic nanoparticles.

6.1 monometallic Au/S15-p, Pd/S15-p and bimetallic AuPd/S15-p catalysts

During the plasma reduction, distinct color change was observed for the samples: from pastel yellow to brown purple for Au/S15-p and from earth yellow to light gray for both Pd/S15-p and AuPd/S15-p, implying the formation of metallic nanostructures over SBA-15 support.

The wide-angle XRD patterns of these samples are shown in Figure 6.1. A broad diffraction peak at ca. 22.4° is observed for all the samples and ascribed to the amorphous silica framework of SBA-15. Au/S15-p exhibits four diffraction peaks at 38.16, 44.30, 64.58, and 77.54°, indexed to (111), (200), (220), and (311) reflections, respectively for the face-centered cubic (FCC) lattice structure of Au (PDF# 65-2870). The peaks are sharp and intense, indicating a good crystallinity of metallic Au. Pd/S15-p shows only one diffraction peak at 39.72° assigned to Pd (111) reflection (PDF# 46-1043) that is weak and broad, indicating the poor crystallinity with structural defects. The average particle size calculated based on (111) reflection using Scherrer formula is 5.8 and 1.6 nm for Au/S15-p and Pd/S15-p, respectively. For bimetallic AuPd/S15-p, reflections assigned to both metallic Au and Pd are clearly seen individually, which rules out the possibility of a single-phase homogeneous Au-Pd alloy. Besides the predominant presence of Au-Pd bimetallic nanoparticles, the probability of sporadically dispersed Au and Pd monometallic nanocrystallites should also be taken into consideration. The diffraction peaks of metal oxides are undetectable, suggesting that the Ar glow

discharge plasma can effectively reduce the metal cation to metallic phase at room temperature [11].

Figure 6.1 XRD patterns of representative Au, Pd and Au-Pd catalysts.

The TEM micrographs of Au/S15-p, Pd/S15-p and AuPd/S15-p and their corresponding particle size distributions are depicted in Figure 6.2. The highly ordered mesoporous structure of SBA-15 is well preserved after precursor impregnation and glow discharge plasma reduction. For Au/S15-p (Figure 6.2a), Au nanorods are formed along the channels of SBA-15, which are uniform in shape with a diameter of ca. 5.9 nm and an aspect ratio of around 4. Spherical Pd nanoparticles are highly dispersed and confined in the SBA-15 channels for Pd/S15-p. The average particle size is determined to be 5.3 ± 0.6 nm, dramatically larger than the average size of single Pd crystalline particles calculated by XRD (1.6 nm), which can be ascribed to the fact that powder XRD is sensitive to the size of coherent domains that can significantly differ from the particle size in the case of multiple crystals composed of smaller primary nanoparticles [20]. The different morphologies of nanostructures (nanorods for Au whereas nanoparticle for Pd) obtained after reducing in glow discharge plasma have been reported by Wang *et al.*

and attributed to the intrinsic properties of different metals, such as surface energy, redox potential, *etc* [12]. Bimetallic AuPd/S15-p also shows spherical shape morphology with a narrow particle size distribution centered at 5.7 nm.

Figure 6.2 TEM results for mono- and bimetallic catalysts: (a) Au/S15-p; (b) Pd/S15-p; (c) AuPd/S15-p; (d) AuPd/S15-H. (1, low-resolution TEM image; 2, HRTEM image; 3, corresponding size distribution).

The HRTEM images are also depicted in Figure 6.2. Au nanorods consist of multiple crystals, showing clear lattice fringes with $d = 0.236$ and 0.205 nm assigned to the (111) and (200) planes of Au, respectively (Figure 6.2a-2), which is in good agreement with XRD results. Pd/S15-p exhibits a fringe distance of 0.227 nm (Figure 6.2b-2) corresponding to Pd(111) plane. Figure 6.2c-2 shows that the bimetallic nanoparticles in AuPd/S15-p retain the FCC lattice structure without the structural incoherency assignable to separate monometallic phases. A subtle phase contrast at the fringe is observed, and the calculated lattice fringes of $d = 0.235$ and 0.203 nm correspond to Au(111) and Au(200) facets, respectively. Surprisingly, no lattice facets assigned to Pd can be determined. The line-scan EDX analysis was carried out in STEM model to further confirm the local composition and element distribution of the bimetallic nanoparticles. The EDX profiles of Au-L α and Pd-L α X-rays are plotted in Figure 6.3a along the line on a representative individual nanoparticle (inset of Figure 6.3a). The particle is ca. 6 nm in diameter, and both Au and Pd are detected, confirming the successful preparation of Au-Pd bimetallic nanoparticles. Different intensity profiles are shown: a volcano-like distribution with maximum at center for Au and a uniform distribution throughout the scanning track for Pd. The intensity of each element is assumed to be proportional to the atomic densities. Similar EDX result was obtained in our previously reported Au-Pd bimetallic catalysts, and denoted as a structure of Pd cluster on Au-rich core [3].

Figure 6.3 The line-scan EDX intensity profiles of a single bimetallic particle of AuPd/S15-p along the line. The inset is the corresponding STEM image.

In addition to the bulk morphology and structure, additional information about the surface components of Au-Pd bimetallic nanoparticles was further derived by XPS measurements. The XPS spectra of $Au4f$, $Pd3d$, $O1s$ and $Si2p$ core levels are shown in Figure 6.4, and the surface compositions are summarized in Table 6.1. For AuPd/S15-p, BEs at 87.3 ($4f_{5/2}$) and 83.5 ($4f_{7/2}$) eV are characteristic of metallic Au while two symmetric peaks at 340.6 ($3d_{3/2}$) and 335.5 ($3d_{5/2}$) eV are assigned to metallic Pd, suggesting the complete reduction of Au and Pd by Ar glow discharge plasma. The expected Au/Pd molar ratio in bulk is 0.54. Nevertheless, AuPd/S15-p shows a significantly decreased ratio of 0.21, implying that the plasma reduced Au-Pd bimetallic nanoparticles are surface-enriched in Pd. Hutchings and co-workers have attributed this Pd surface-enrichment to the formation of a Pd(shell)-Au(core) structure [8]. The characteristic peaks for $O1s$ and $Si2p$ exhibit consistent BEs with SiO_2 . The surface O/Si atomic ratio is 2.69 which is higher than the bulk stoichiometric ratio of 2.0 due to the coverage of

surface hydroxyl groups [21].

Table 6.1 Surface compositions calculated from XPS results of representative samples.

Sample	Surface atoms percentage ^a (at%)				Surface Au/Pd ratio(at%)	Surface O/Si ratio(at%)	Relative abundance of Pd ⁰ /Pd ²⁺ (at%)	
	Au	Pd	O	Si			Pd ⁰	Pd ²⁺
AuPd/S15-p	0.060 (0.56)	0.27 (1.47)	72.67	27.00	0.21	2.69	100.00	0
AuPd/S15-H	0.10 (1.01)	0.19 (1.03)	73.18	26.53	0.53	2.76	100.00	0
AuPd/S15-pR	0.10 (1.05)	0.29 (1.56)	73.01	26.59	0.36	2.75	59.29	40.71

^a values in parentheses are wt.%.

To summarize above XRD, TEM, HRTEM, EDX and XPS analyses, a Pd-rich shell/Au-rich core structure can be proposed for AuPd/S15-p catalyst. The so-called “geared step-cycled reduction” mechanism due to the different redox potentials of Au and Pd may explain the formation of such structure [3, 22]: during the plasma reduction of Pd and Au cations, the preferential reduction of Au is favored via an electron transfer from Pd to Au due to the higher electron-negativity of Au. Pd²⁺ precursor acts as an electron-mediate and accelerates the reduction of Au cations. After the coalescence and growth of Au clusters, Pd cations are adsorbed on Au surface and further reduced, affording a Pd shell/Au core structure. In addition, a reasonable explanation to the expansion of Pd facets is the pseudomorphically epitaxial growth of Pd on Au-rich core, which has been suggested by Hori and co-workers [23].

Figure 6.4 XPS spectra of AuPd/S15, AuPd/S15-H and AuPd/S15-pR: (a) Au4f; (b) Pd3d; (c) O1s; (d) Si2p core levels.

Figure 6.5 shows CO adsorbed infrared spectra at room temperature on various catalysts. For Au/S15-p, the doublet at 2172 and 2119 cm^{-1} due to gas-phase CO is observed upon introducing CO. CO linearly bonded to low-coordinated metallic Au sites (step sites over the Au surfaces and step sites at

the interface of Au and the support) should show a characteristic peak at ca. 2100 cm^{-1} [24]; and the residual Cl^- after impregnation may change the electron properties of Au and shift this adsorption peak to a higher frequency [25]. Herein, the band at 2119 cm^{-1} will be ascribed as the combination of gaseous CO and CO linearly adsorbed on step sites of metallic Au^0 [24]. After removing gas-phase CO, this absorbance is red-shifted to 2117 cm^{-1} with a substantial asymmetric tailing in the high-frequency region, suggesting a wide distribution of CO sites with different adsorption strengths [26].

Three distinct bands are clearly observed for Pd/S15-p after exposing to CO: 1) the band at 2089 cm^{-1} attributed to linear carbonyls on (111) facet of Pd particles (designed as L); 2) a band at 1990 cm^{-1} assigned to 2-fold bridged carbonyls on (100) facet of Pd particles (designed as B_1); 3) a broad band at 1948 cm^{-1} corresponding to 2-fold bridged carbonyls on (111) facet of Pd particles (designed as B_2). The intensities of these absorbencies significantly increase at higher CO coverage. After 20 min of CO exposure, the intensities of three bands no longer change, indicating the saturation of CO adsorption on Pd particles. Upon purging under He, the characteristic peaks assigned to gaseous CO completely disappear after 5 min. The intensities of other bands also decrease evidently and red-shift to lower frequencies due to the decreased CO coverage. After purging with He for 30 min, only the features of L and B_2 remain, suggesting the preferential and more stable carbonyls adsorption on Pd (111) facets compared to Pd (100) facets. Furthermore, no band for Pd^{2+} (between 2160 and 2116 cm^{-1}) or Pd^+ (between 2114 and 2140 cm^{-1}) can be seen, confirming the exclusive presence of surface metallic Pd species in Pd/S15 [27].

AuPd/S15-p exhibits CO-DRIFT spectra characteristic of Pd, implying that

Au may be covered (at least partially covered) by Pd in the bimetallic nanoparticles, which further suggests the possibility of Pd-rich shell/Au-rich core structure. After purging under He for 30 min, L and B₁ CO bands red-shift from 2090 to 2085 and from 1944 to 1939 cm⁻¹, respectively compared to monometallic Pd/S15-p, which can be contributed by either a geometric or an electronic effect [28]. Firstly, Pd crystallites form small islands and rough surfaces in the presence of Au core, leading to a weaker lateral interaction between adsorbed CO molecules (*i.e.*, decreased dipole–dipole coupling in the adlayer). Secondly, due to the larger electron negativity of Au than Pd, Pd donates electrons to Au and becomes electron-deficient, which is compensated via an increased back donation in the 2π* anti-bonding orbitals of adsorbed CO molecules. Therefore, not only the Pd ensemble size has been affected, but also the electronic properties of Pd have been modified in the presence of Au. The synergistic effect between Au and Pd on the local structure and active site distribution of bimetallic nanoparticles can also be semi-quantitatively reflected by the relative intensity of bridge CO to linear CO ((B₁+B₂)/L) [19]. To exclude the interference of gaseous CO, the CO-DRIFT spectra of CO-desorption after 30 min He purging was employed to analyze the peaks. Outgassing at room temperature completely depletes the B₁ band, and only the area ratio of B₂/L is calculated, showing 1.65 and 1.43 for Pd/S15-p and AuPd/S15-p, respectively. CO is preferentially bound linearly (L) on low-coordinated Pd atoms and the B/L ratio decreases for small particles due to the larger fraction of low-coordinated surface atoms [29]. In this study, although it shows a slightly larger particle size than Pd/S15-p (5.3 and 5.7 nm for Pd/S15-p and AuPd/S15-p, respectively), AuPd/S5-p possesses more exposed Pd atoms of low-coordination (edge/corner sites), suggesting that the Pd nano-crystallites

undergo a major restructure, leading to a large exposure of coordination-unsaturated Pd atoms.

The selective oxidation of benzyl alcohol with molecular O₂ was employed as a chemically probed reaction to examine catalytic performances of the plasma reduced mono- and bimetallic catalysts. In the absence of catalysts, only 7.5% of benzyl alcohol converts due to non-catalytic oxidation. The SBA-15 support does not show any catalytic activity (8.1% conversion). The evolution of the catalytic performance with reaction time was studied and the results are illustrated in Figure 6.6. Monometallic Au catalyst possesses poor activity and quickly deactivates after 4 h while both Pd/S15-p and AuPd/S15-p catalysts show monotonically increased benzyl alcohol conversions. After reacting for 8 h, only 25.7% conversion can be achieved over Au/S15-p and Pd/S15-p can convert 83.6% benzyl alcohol. AuPd/S15-p exhibits an excellent catalytic activity, showing 100% conversion of benzyl alcohol. The plots in Fig. 6a are fitted with 1st-order reaction kinetics and the rate constants are listed in Table 6.2. AuPd/S15-p shows a rate constant k of $0.50 \pm 0.05 \text{ h}^{-1}$, which is 12.5-fold of Au/S15-p (0.04 ± 0.01) and 2-fold of Pd/S15-p (0.28 ± 0.02). The catalytic activity is also represented using $q\text{TOF}$ (Figure 6.6c). After the first 0.5 h of reaction, AuPd/S15-p shows a $q\text{TOF}$ of ca. 27000 h^{-1} , which is more than twice of monometallic Pd and Au catalysts. Therefore, besides the excellent long-term stability, AuPd/S15-p also shows a high catalytic activity.

Figure 6.5 DRIFT spectra of CO adsorbed at 25 °C on Au/S15-p, Pd/S15-p, AuPd/S15-p and AuPd/S15-H. Sample exposed to 1.1 kPa CO for (a) 1 min, (b) 5 min, (c) 10 min, (d) 20 min, (e) 30 min; and purged with He for (f) 1 min, (g) 5 min, (h) 10 min, (i) 20 min, (j) 30 min.

Figure 6.6 The time-activity profile for selective benzyl alcohol oxidation over Au/S15-p, Pd/S15-p and AuPd/S15-p catalysts: (a) benzyl alcohol conversion; (b) benzaldehyde selectivity; (c) q_{TOF} ; (d) benzaldehyde yield. Reaction conditions: benzyl alcohol/metal = 250/1 mmol/mg; O₂, 20 mL min⁻¹; temperature, 433 K.

The selectivity toward benzaldehyde differs remarkably among these catalysts (Figure 6.6b). Benzaldehyde is produced dominantly (selectivity > 98%) over Au/S15-p during the first 3 h, followed by a slightly decreased selectivity due to the over-oxidation of benzaldehyde to benzoic acid, which occurs independently to the intervention of catalyst [30]. Pd/S15-p shows a low benzaldehyde selectivity of 59.0% after the first 0.5 h of reaction, with tremendous amounts of toluene as by-product. The selectivity increases along the reaction time and reaches its maximum at 3 h, and further deteriorates due to formation of benzoic acid. After 8 h of reaction, only 53.2% benzaldehyde selectivity remains, accompanied by the large quantity of benzoic acid due to over-oxidation. AuPd/S15-p shows a good

selectivity profile in between monometallic Au and Pd catalysts, which can be well maintained at high conversion up to 8 h.

The effect of reaction temperature was also examined for these catalysts ranged from 120 to 160 °C. In general, the elevated temperature leads to increased reaction rate. The Arrhenius plot is shown in Figure 6.7. The determined pre-exponential factors are 1.44E5, 5.95E7, and 2.87E1 for Au/S15-p, Pd/S15-p and AuPd/S15-p, respectively. The frequency factor A reflects the total number of collisions per unit time while rate constant k is the number of collisions that result in a reaction. Therefore, the ratio of k to A (k/A) approximately is the number of effective active sites for reactions. As shown in Table 6.2, A is large while k is rather small for Au/S15-p, implying that most collisions cannot initiate the reaction due to insufficient effective active sites. In contrast, Pd/S15-p shows the largest k/A ratio due to the abundance of effective active sites. AuPd/S15-p possesses the moderate number of active sites. The information derived from k/A ratio complements the *true* activation energy E_a measured according to the rate constant k (as listed in Table 6.2). Au/S15-p exhibits a remarkably high E_a of 75.7 ± 2.9 kJ/mol, demanding high energy input to initiate the reaction, which is consistent with its low catalytic activity. In contrast, the E_a for Pd/S15-P is extremely low (16.7 ± 0.7 kJ/mol), suggesting a facilely initiated reaction. Nonetheless, mass-transport limitation and reactant diffusion resistance may be concerned when the surface reaction occurs much faster than reactant adsorption and/or product desorption [3]. The calculated E_a for AuPd/S15-p (45.1 ± 4.2 kJ/mol) is moderate to readily initiate the reaction as well as to obtain an optimal reaction-diffusion balance. Additionally, this E_a is remarkably higher than that of SBA-16 supported Au-Pd catalyst (16.7 kJ/mol) in Chapter 4 [3], indicating that the ordered

arrangement of mesochannels of SBA-15 exhibits less resistance for electric charger and ion diffusion in comparison with that of SBA-16.

Figure 6.7 Arrhenius plot of plasma reduced Au, Pd and Au-Pd catalysts.

To clarify the origin of toluene and reaction mechanism, we studied the catalytic performance in 1 h of reaction time over these three catalysts in a N₂ atmosphere and the results are depicted in Figure 6.8. When benzyl alcohol was exposed to the anaerobic conditions, benzaldehyde and toluene were both produced, implying a dehydrogenation mechanism in which benzaldehyde formation occurs in the absence of oxidant. Au catalyst shows the highest selectivity (>65%). For Pd/S15-p, 43.4% of benzaldehyde and 56.6% toluene are produced after first 10 min. Benzaldehyde is generated as a subordinate component until 50 min of reaction, accompanied by a large amount of toluene. Mixing Au with Pd can remarkably suppress the formation of toluene over Pd catalyst, implying that toluene is generated via either a hydrogen transfer or an oxygen transfer mediated by surface-enriched Pd over AuPd/S15-p with a Pd-rich shell/Au-rich core structure [30]. Fig. 6f shows that toluene and benzaldehyde are

generated almost in equimolar amounts in the initial stage of reaction over AuPd/S15-p, implying that the disproportionation of benzyl alcohol occurs even at very low conversions. The initial rates, which are determined from the slopes of the conversion curves at zero conversions under aerobic (O₂) and anaerobic (N₂) conditions are summarized in Table 6.2. It is noteworthy that for these three catalysts, the initial rates are one order of magnitude higher under O₂ than N₂, indicating the essential role of O₂ in benzyl alcohol oxidation. Pd itself shows comparable r_0 to Au-Pd bimetallic catalyst under N₂, further suggesting that Pd is dominantly responsible for the reaction over AuPd/S15-p. After introducing O₂, Au-Pd bimetallic nanoparticles remarkably enhance the initial rate, showing an increasing rate of benzyl alcohol disappearance and benzaldehyde appearance.

Table 6.2 The average particle size and kinetic parameters of benzyl alcohol oxidation under anaerobic and aerobic conditions^a.

Catalyst	Particle size ^b (nm)	Ea ^c (kJ/mol)	A ^c (h ⁻¹)	Rate constant k^d (h ⁻¹)	Initial rate r_0 (mol/h)	
					Anaerobic	Aerobic
Au/S15-p	5.9(D)	75.7	5.95E7	0.04	0.0009	0.010
Pd/S15-p	5.3	16.7	2.87E1	0.28	0.0027	0.022
AuPd/S15-p	5.7	45.1	1.44E5	0.50	0.0042	0.039
AuPd/S15-H	5.8	- ^e		0.36	-	0.025
AuPd/S15-pO	13.9	-		0.28	0.0024	0.028
AuPd/S15-pR	6.7	-		0.33	0.0021	0.033

^aReaction conditions: benzyl alcohol/metal = 250/1 mmol/mg; O₂(N₂), 20 mL min⁻¹; temperature, 160 °C.

^bdetermined from TEM results.

^c determined from Arrhenius plots $\ln k = -E_a/RT + \ln A$.

^d k is determined for reaction under aerobic conditions.

^e not determined.

Figure 6.8 The catalytic behaviors for benzyl alcohol oxidation under N_2 atmosphere: (a) Au/S15-p; (b) Pd/S15-p; (c) AuPd/S15-p. Reaction conditions: benzyl alcohol/metal = 250/1 mmol/mg; N_2 , 20 mL min⁻¹; temperature, 433 K.

6.2 plasma reduction vs. H_2 thermal-reduction

Au-Pd bimetallic catalyst by the conventional thermal-reduction in a

hydrogen atmosphere was also prepared and denoted as AuPd/S15-H. The XRD pattern of AuPd/S15-H catalyst, as depicted in Figure 6.1, is similar to that of AuPd/S15-p. The (111), (200), (220), and (311) reflections of Au and (111) reflection of Pd are clearly identified, suggesting the FCC lattice structure of AuPd/S15-H. However, the peak intensity of AuPd/S15-H is much lower compared to plasma reduced sample, implying the unsatisfactory crystallinity after H₂ reduction. No characteristic peaks of PdO can be observed.

The morphology of AuPd/S15-H bimetallic nanoparticles is more directly shown in the TEM micrograph in Figure 6.2d-1. Spherical shape nanoparticles are highly dispersed on SBA-15, and the average particle diameter of AuPd/S15-H (ca. 5.8 nm) is similar to that of AuPd/S15-p. Nonetheless, the particle size distribution is remarkably broad. A noticeable fraction of particles is smaller than 2 nm, as well as many particles are larger than 12 nm (Figure 6.2d-3). HRTEM results show that the particle exhibits a decahedral multiply twinned structure for AuPd/S15-H, and each twinned part maintains the FCC structure. Figure 6.2d-2 presents two twinned boundaries of a multiply twinned particle, which is distinctly different from the Pd-rich shell/Au-rich core structure of AuPd/S15-p. The lattice fringe assigned to Au(111) facet is determined as 0.236 nm that is consistent with the value derived from XRD pattern.

The surface compositions of AuPd/S15-H were also examined by XPS measurements. As depicted in Figure 6.4, AuPd/S15-H exhibits similar XPS spectra of Au4*f*, Pd3*d*, O1*s*, and Si2*p* core levels compared to AuPd/S15-p. The bimetallic nanoparticles after H₂ thermal-reduction consist exclusively of metallic Au⁰ and Pd⁰ species. The surface Au/Pd ratio of AuPd/S15-H is determined as 0.53, which is almost identical to the nominal bulk ratio (0.54), suggesting the absence

of preferential enrichment of Au or Pd on the surface. We speculate a possibility of aggregated bimetallic nanoparticle with irregular Au-Pd distribution. The surface O/Si atomic ratio is 2.76, which is also contributed by the surface coverage of hydroxyl groups [21].

CO-adsorbed DRIFT results are illustrated in Figure 6.5. Despite similar to the CO-DRIFT spectra of AuPd/S15-p, the IR bands of AuPd/S15-H are sharper, implying a stronger adsorption of CO, which can be attributed to either smaller particle size or weaker metal-support interaction [13]. Upon introducing CO, both linear- (L) and bridge-bound (B_1 and B_2) CO bands appear. After 30 min He purging, B_1 disappears, indicating the unstable carbonyls adsorption on Pd (100) facet. L band is centered at 2089 cm^{-1} , which is in accordance with AuPd/S15-p. Nonetheless, B_2 shows a higher frequency (1946 cm^{-1}) compared to AuPd/S15-p, which is attributed to the geometric or electronic effect. The relative intensity of bridge-bound CO to linear-bound CO ($(B_1+B_2)/L$) of AuPd/S15-H is determined as 0.8, suggesting the large abundance of low-coordinated Pd atoms due to the noticeable fraction of small particles that contribute dominantly to the linearly binding CO.

The catalytic behavior of AuPd/S15-H was examined for the selective oxidation of benzyl alcohol under aerobic conditions, as shown in Figure 6.9. Although AuPd/S15-H possesses similar average particle size, the catalytic activity is poorer compared to AuPd/S15-p. The rate constant and the initial rate are determined as $0.36\pm0.04\text{ h}^{-1}$ and 0.025 mol/h , respectively (Table 6.2). Wang and co-workers have proposed that benzyl alcohol molecule is adsorbed via such a conformation that the benzene ring is parallel to the terrace sites while the β -H is attached to the edge/corner sites, *i.e.*, the adsorption needs terrace atoms while the

β -H cleavage requires the edge/corner sites. Thus, a balance of terrace to edge/corner atoms is critical, which favors both adsorption of benzyl alcohol and the subsequent β -H cleavage [31]. It is noteworthy the selectivity toward benzaldehyde is also poor over AuPd/S15-H and the best selectivity obtained at 3 h (82.4%) is ca. 15% lower than AuPd/S15-p. A large amount of benzoic acid is produced and only 16% selectivity toward benzaldehyde remains after 8 h. It was proposed that only selected sites allow the desorption of benzaldehyde, implying that the benzaldehyde selectivity is dependent on the particle size as well as the active site distribution [32]. AuPd/S15-H has a large amount of particles small in diameter, which show high oxygen heat of adsorption, *i.e.*, strong affinities of oxygen, and are prone to oxygen poisoning. According to the oxidative dehydrogenation reaction mechanism, the metal surfaces will be covered by the dehydrogenation products, such as organic substrates/intermediates, oxygen and hydrogen. With the reaction proceeds, the concentration of benzyl alcohol decreases and excess amounts of oxygen occupies the metal surfaces, leading to the over-oxidation of benzyl alcohol to benzoic acid and thereby the sharply decreased selectivity.

6.3 Effect of post-treatment of AuPd/S15-p

Above-mentioned results have verified the superiority of Ar glow discharge plasma treatment to the conventional H₂ thermal reduction. To further understand the nature of bimetallic nanoparticles formed under plasma reduction, we introduced the post-treatment to the as-synthesized AuPd/S15-p, *i.e.*, O₂ calcination of AuPd/S15-p (AuPd/S15-pO) followed by a H₂ thermal reduction at 500 °C for 4 h (AuPd/S15-pR). The effect of post-treatment was examined by the following characterizations and catalytic tests.

Figure 6.9 The activity profile for selective benzyl alcohol oxidation using molecular O₂ over AuPd/S15-p and AuPd/S15-H: (a) benzyl alcohol conversion; (b) benzaldehyde selectivity. Reaction conditions: benzyl alcohol/metal = 250/1 mmol/mg; O₂, 20 mL min⁻¹; temperature, 433 K.

The wide-angle XRD patterns of AuPd/S15-pO and AuPd/S15-pR are depicted in Figure 6.1. In both samples, Au exists as metallic phase with a slight shift towards high angle for the characteristic peaks, implying a shrunken lattice constant and possible lattice contraction. For AuPd/S15-pO, the peaks assigned to metallic Pd⁰ completely disappear. An intense peak at 33.76° and four weak diffraction peaks at 41.92, 54.58, 60.16 and 71.48° appear, which are indexed to (101), (110), (112), (103), and (211) reflections of tetragonal PdO lattice (PDF #

41-1107). Therefore, PdO is the predominant phase after re-oxidation under O₂ atmosphere. The diffraction peaks are sharp and intense, suggesting the aggregation of PdO particles to a certain extent during the oxidative thermal treatment. For AuPd/S15-pR, a shoulder peak at 39.5° assigned to Pd(111) plane appears. Surprisingly, the diffraction peaks of PdO only become weak and broad rather than disappear, implying the incomplete reduction of PdO. This is in contrast to the exclusive presence of metallic Pd⁰ phase for monometallic Pd/S15 synthesized via the same preparation procedure in the previous report [11], and can be attributed to the synergistic interaction between Pd and Au. Introducing Au may effectively hinder the decomposition of PdO to Pd at high temperatures [33]. Doping Au with Pd is also suggested to “protect” TiO₂ support under reducing atmosphere [34]. From the XRD pattern, we suggest that the structure of the nanoparticles in AuPd/S15-pR (Au, Pd and PdO) is ill-defined, nonetheless, the presence of homogeneous phase of Au-Pd alloy can be ruled out due to the individual peaks for Au and Pd.

The nanoparticle morphology and structure of AuPd/S15-pO and AuPd/S15-pR, as well as their corresponding size distributions, are directly shown in Figure 6.10. Only large particles exist for AuPd/S15-pO (13.9±3.3 nm), suggesting the substantial aggregation of Au and/or PdO nanoclusters. HRTEM image in Figure 6.10b-2 shows the lattice constants $d = 0.235$ and 0.266 nm, corresponding to Au(111) and PdO(101) planes, respectively. After H₂ re-reduction, AuPd/S15-pR shows an improved particle size distribution. Lattice facets corresponding to Au(111) ($d=0.233$ nm) and Pd(111) ($d=0.225$ nm) can be observed in Figure 6.10c-2. Figure 6.11 shows the EDX profiles of Au-L α and Pd-L α X-rays plotted along the line on a representative individual nanoparticle

over AuPd/S15-pR. In contrast to AuPd/S15-p, Pd in AuPd/S15-pR displays a similar profile compared to Au and the intensity along the entire line scans is strong. Therefore, Au and Pd should co-exist in bimetallic nanoparticles with Pd/PdO clusters covering on the small Au core.

Figure 6.10 TEM results for different bimetallic AuPd catalysts: (a) AuPd/S15-p; (b) AuPd/S15-pO; (c) AuPd/S15-pR. (1, low-resolution TEM image; 2, HRTEM image; 3, corresponding size distribution).

Figure 6.11 The line-scan EDX intensity profiles of a single bimetallic particle of AuPd/S15-pR along the line. The inset is the corresponding STEM image.

AuPd/S15-pR shows similar XPS spectra of Au4*f*, O1*s*, and Si2*p* core levels compared to AuPd/S15-p, as depicted in Figure 6.4. The Pd3*d* spectrum consists of two asymmetric peaks attributed to Pd3*d*_{3/2} and Pd3*d*_{5/2} core levels (Figure 6.4b). In addition to the characteristic peaks assigned to metallic Pd⁰, two small peaks around 341.3 and 336.4 eV corresponding to Pd²⁺ species appear after deconvolution. The calculated abundance of surface Pd²⁺ is 40.71%. The Au4*f* spectrum shows that Au remains in metallic phase. The peaks of both metallic Au⁰ and Pd⁰ shift to lower Bes due to the increased number of Au-Pd bonds as the Au core becomes smaller, which is consistent with the EDX results. After H₂ re-reduction, the residual oxide species on the topmost Pd layer may induce the inner Pd atoms at the Au-Pd interface partially positive-charged, which significantly affects the Au-Pd bonding strength and thereby imposes strong impact on the bimetallic synergistic interaction. The surface Au/Pd atomic ratio of AuPd/S15-pR (0.36) is larger than that of AuPd/S15-p (0.21), which corresponds

to a Pd surface-enrichment with larger abundance of surface Au⁰ species.

CO-adsorbed DRIFT spectra of AuPd/S15-pO and AuPd/S15-pR are illustrated in Figure 6.12. For AuPd/S15-pO, besides the gaseous CO band at 2172 cm⁻¹, only two adsorption bands at 2113 and 1956 cm⁻¹ appear. The higher wavenumber band can be assigned to CO adsorbed on Pd²⁺ sites and the lower frequency band is due to Pd⁺-CO-Pd⁺ species [35]. Both bands show a remarkable red-shift to 2168 and 1948 cm⁻¹, respectively when purging under He for 5 min, which can be assigned to L and B₂ bands of CO adsorption on metallic Pd⁰ sites formed due to the slow reduction of PdO during CO adsorption and He outgasses (The peaks assigned to gaseous CO₂ appear and are not shown here). Moreover, both bands undergo slight blue-shift compared to AuPd/S15-p, which is contributed by the electronic effect associated with weakened surface CO bond, i.e., the compression of CO adlayer by surface oxygen species (PdO) leads to higher frequencies. The band B₁ is undetectable, implying the absence of exposed Pd(100) facets, which is consistent with the exclusive presence of PdO after O₂ re-oxidation. The calculated relative intensity of bridge-bound to linear-bound CO (B/L=5.55) is higher than AuPd/S15-p (1.43), indicating that the bimetallic nanoclusters in AuPd/S15-pO dominantly consist of close-packed planes with few low-coordinated atoms due to the large particle and poor dispersion (13.9±3.3 nm). After re-reduction, AuPd/S15-pR shows similar CO-DRIFT spectra compared to AuPd/S15-p. Notably, B₁ band appears upon introducing CO gas, which suggests the exposure of Pd(100) facets and confirms the atomic re-arrangement after re-reduction. The B/L value of AuPd/S15-pR is 1.81, which is slightly higher than that of AuPd/S15-p due to the slight increase in the particle size (6.7±0.9 nm).

Figure 6.12 DRIFT spectra of CO adsorbed at 25 °C on AuPd/S15-pO and AuPd/S15-pR, with the results of AuPd/S15-p included for comparison. Sample exposed to 1.1 kPa CO for (a) 1 min, (b) 5 min, (c) 10 min, (d) 20 min, (e) 30 min; and purged with He for (f) 1 min, (g) 5 min, (h) 10 min, (i) 20 min, (j) 30 min.

The catalytic activities of AuPd/S15-pO and AuPd/S15-pR are compared with that of AuPd/S15-p and shown in Figure 6.13. The conversion plots are fitted with 1st-order reaction kinetics, showing the rate constants k as 0.28 ± 0.04 and 0.34 ± 0.08 h⁻¹ for AuPd/S15-pO and AuPd/S15-pR, respectively. The initial rates r_0 are 0.028 and 0.033 for these two samples, as listed in Table 6.2. Re-oxidation and subsequent reduction show inferior catalytic performances to plasma-reduced AuPd/S15-p catalyst due to the modified morphology and surface chemistry of catalyst after post-treatments. O₂ re-oxidation of AuPd/S15-p leads to an apparent deterioration of activity, particularly a depressing initial reaction rate. Metallic Pd⁰ is suggested to be more active than PdO and predominantly contribute to the high activity [36]. Our previous study also demonstrated that the initial reaction activity is intimately related to the surface Pd⁰ concentration [4]. After re-oxidation, AuPd/S15-pO consists exclusively of Au and PdO species. Consequently, an induction period is required to transform PdO into metallic Pd nanoparticles, which accounts for the low initial activity. The slightly higher selectivity toward benzaldehyde over AuPd/S15-pO is in accordance with the poor activity. Subsequent H₂ re-reduction can retrieve a comparable initial activity with AuPd/S15-p, implying the existence of surface Pd⁰ species. However, the conversion reaches a plateau after 2 h, suggesting a rapid deactivation and declined stability, which is contributed by lower hydrogen uptake due to the large abundance of surface Au in AuPd/S15-pR than AuPd/S15-p. The β -H elimination producing carbonyl and surface hydride is known as the rate-limiting step in the dehydrogenation of alcohols. Therefore, the weakened capability to adsorb surface metal-hydride components may be responsible for the poor long-term stability. Nonetheless, the less abundance of surface hydride species contributes to the high

benzaldehyde selectivity by effectively suppressing the hydrogenolysis of benzyl alcohol to toluene, as shown in Figure 6.13b.

Figure 6.13 The time-activity profile for selective benzyl alcohol oxidation over AuPd/S15-pO and AuPd/S15-pR catalysts: (a) benzyl alcohol conversion; (b) benzaldehyde selectivity. Reaction conditions: benzyl alcohol/metal = 250/1 mmol/mg; O₂, 20 mL min⁻¹; temperature, 433 K.

The catalytic performances in N₂ over AuPd/S15-pO and AuPd/S15-pR are recorded within 1 h reaction time, as depicted in Figure 6.14. A dehydrogenation mechanism is verified due to the formation of benzaldehyde in the absence of oxidant. As the solely detectable by-product over both catalysts, toluene is initially produced in a moderate amount rather than equimolar to benzaldehyde, suggesting

that after post-treatments (re-oxidation and/or re-reduction), the formation of toluene probably undergoes a hydrogenolysis step rather than disproportionation of benzyl alcohol, which is suppressed by less amounts of surface metal-hydride. As listed in Table 6.1, the initial rates r_0 over two catalysts under anaerobic conditions are similar (AuPd/S15-pO, 0.0024 mol/h; AuPd/S15-pR, 0.0021 mol/h), which is only half of that of AuPd/S15-p. The decreased exposure of Pd may account for the low initial activity since Pd has been evidenced to be dominantly responsible in Au-Pd bimetallic catalyst.

Figure 6.14 The time-activity profile for selective benzyl alcohol oxidation under anaerobic condition (a) AuPd/S15-pO; (b) AuPd/S15-pR. Reaction conditions: benzyl alcohol/metal = 250/1 mmol/mg; N_2 , 20 mL min⁻¹; temperature, 433 K.

6.4 Discussions

The structures of Au, Pd and Au-Pd catalysts proposed previously are summarized in Scheme 6.1. AuPd/S15-p shows Pd-rich shell/Au-rich core structure with surface-enrichment of coordination-unsaturated Pd atoms. The superior catalytic performance of AuPd/S15-p to monometallic Au and Pd catalysts can be addressed from the following two aspects. (i) The changed interatomic distance of Pd on the surface may have both geometric and electronic effects. Au can disperse/isolate Pd sites, preventing oxygen poisoning of Pd in the liquid-phase oxidation [10]. Au with higher electron negativity also withdraws electron from Pd atoms, leading to an enhanced interaction of Pd atoms with the substrate and thereby improved activity and selectivity. Recently, it has also been reported that the presence of nanocontacts triggers electron transfer and localized charge redistribution in the contact region, which are highly attractive to charged organic molecules, resulting in the improvement of organic transformations [37]. (ii) As suggested by Mori *et al.*, low-coordination Pd surface sites (edges and/or corners) are more active than the highly coordinated terrace sites for β -H elimination, which is the rate-limiting step in the oxidative dehydrogenation of alcohols. In this study, AuPd/S15-p with more surface coordination-unsaturated Pd atoms as evidenced by CO-DRIFT measurements shows a strong positive effect towards β -H cleavage, thus leading to a high activity.

Scheme 6.1 Sketch diagram of preparation procedure of Au, Pd, and Au-Pd catalysts with their corresponding structures.

Compared to AuPd/S15-p, both inferior structure and catalytic activity were observed over AuPd/S15-H prepared by conventional hydrogen thermal reduction (Scheme 6.1 and Figure 6.9). The advantage of Ar glow discharge plasma reduction over H₂ thermal reduction may be attributed to its plausible mechanism involving two processes: (i) a direct process, in which the high energy species generated by the plasma, such as electrons and ions, directly reduce the metal ions through a recombination process; (ii) an indirect process involving the excitation (dissociation and ionization) of the chemisorbed water molecular to generate active species (*e.g.*, e_{aq}^-) with strong reducibility, which is normally contributed for non-hydrogen glow discharge treatment [38]. In both processes, metallic nanoparticles can be obtained with regular and uniform distribution.

Au-Pd bimetallic catalysts are speculated to undergo different atomic arrangements during Ar glow discharge plasma treatment at room temperature and H₂ thermal reduction at elevated temperature. Meanwhile, we admit that the

catalyst after plasma reduction may be unstable and undergo a subtle change once it is exposed in the air. Due to the limitation of experimental conditions, we cannot follow the *in-situ* plasma reduction process at this juncture and obtain the real-time information of catalyst. Therefore, we introduced post-treatment processes (further O₂ re-oxidation and H₂ re-reduction) on both AuPd/S15-p and AuPd/S15-H, and carried out control experiments for the corresponding Au-Pd catalysts. The structural information is illustrated in Figure 6.1. AuPd/S15-H and AuPd/S15-HR present similar XRD patterns, indicating the “stable” configuration of bimetallic nanoparticles formed by H₂ thermal reduction at high temperature. In contrast, the bimetallic Au-Pd nanoparticles in AuPd/S15-p experience a structural transformation from a Pd-rich shell/Au-rich core structure to a cluster-in-cluster structure. Their catalytic performances are also compared. As shown in Figure 6.15(a), the plots of both conversion and selectivity almost coincide for AuPd/S15-H and AuPd/S15-HR. Surprisingly, the plots in Figure 6.15(b) exhibit the dramatic difference between AuPd/S15-p and AuPd/S15-pH. After post-treatment, the selectivity increases from 67.7% to 81.5% during the first 0.5 h whereas the conversion decreases from 69.0% to 51.0% after 8 h. These evidences indirectly imply that during the Ar glow discharge plasma reduction, the bimetallic nanoparticles undergo a different atomic arrangement of surface atoms, reaching a highly active but “unstable” structure which can be readily affected by post-treatment.

Figure 6.15 Catalytic performance of Au-Pd catalysts: (a) AuPd/S15-H and AuPd/S15-HR; (b) AuPd/S15-p and AuPd/S15-pR.

The yield over H_2 -reduced AuPd/S15-H is plotted in Figure 6.16(a). Compared to AuPd/S15-p, AuPd/S15-H exhibits a slowly increasing and inferior yield, confirming the advantage of plasma reduction to conventional H_2 thermal reduction. The effect of post-treatment (O_2 re-oxidation and H_2 reduction) on the yield is also studied. For H_2 -reduced Au-Pd catalysts before and after post-treatment, the plots almost coincide. However, a large difference is observed between AuPd/S15-p and AuPd/S15-pR. Apparently, the catalytic behavior of the bimetallic nanoparticles undergone plasma reduction is superior but can be readily affected by post-treatment, indicating a highly active but “unstable” bimetallic

nanoparticle configuration.

Figure 6.16 Yield of benzaldehyde over Au-Pd catalysts: (a) AuPd/S15-H and AuPd/S15-HR; (b) AuPd/S15-p and AuPd/S15-pR. Reaction conditions: benzyl alcohol/metal = 250/1 mmol/mg; O₂, 20 mL min⁻¹; temperature, 433 K.

6.5 Conclusions

Bimetallic Au-Pd nanoparticles supported on SBA-15 mesoporous materials were prepared by Ar glow discharge plasma reduction. The size of metal nanostructure (diameter of metal nanoparticles/nanorods) can be effectively controlled and tailored by the highly ordered mesopores of SBA-15 silica. Adding

Au into Pd to form bimetallic Au-Pd nanocomposites well retains the morphology of spherical nanoparticles with a similar particle size distribution. As a green, efficient and safe reduction method, the plasma reduction outperformed the conventional H₂ thermal reduction, showing uniform particle dispersions and size distributions. Characterization results suggested a Pd-rich shell/Au-rich core structure with abundant surface coordination-unsaturated Pd atoms for the effectively reduced Au-Pd bimetallic nanoparticles, which accounted for the good catalytic activity compared to Au and Pd monometallic catalysts in the selective oxidation of benzyl alcohol. At 1 h of reaction, AuPd/S15-p shows a conversion of 47.4% and TOF of 16375 h⁻¹. We believed that the particle nucleation and growth mechanism in the plasma reduction process is different from H₂ thermal reduction, affording modified morphology and surface chemistry of metal nanoparticles. Further oxidation and re-reduction of plasma reduced Au-Pd catalyst resulted in the atomic re-arrangement of nanoparticles, leading to an inferior catalytic performance.

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Chapter 7 Conclusions and Future Perspectives

7.1 Conclusions

In this thesis, the selective oxidation of aromatic alcohols to aldehydes and ketones, particularly benzyl alcohol to benzaldehyde, was tackled to investigate the effect of metal nanoparticle confinement on the catalytic activity over supported noble metal catalysts with particular highlights on the interactions between both metal-metal and metal-support. The primary results and findings are summarized in this chapter.

Highly ordered SBA-16 silica material with cage-like mesopores was synthesized and employed to effectively confine the formation of Au-Pd bimetallic nanoparticles. Surface-functionalization of SBA-16 showed great impact on the catalytic performance and APS-functionalized SBA-16 was selected as the best support. The characterization analysis suggested the formation of alloyed bimetallic nanoparticles with Pd cluster-on-Au-cluster crystalline structure. These highly dispersed Au-Pd bimetallic nanoparticles with the mean diameter around 6 nm showed excellent catalytic performance in catalyzing the selective solvent-free oxidation of a variety of aromatic alcohols and maintained good catalytic stability after recycling.

The limited enhancement on the catalytic activity of Au-Pd bimetallic catalysts compared to Au and Pd monometallic catalysts was attributed to the large resistance of mass transfer in the mesopores of SBA-16 support. Herein, TUD-1 mesoporous silicas were further employed as support. A series of Pd catalysts supported on TUD-1 functionalized with various organosilanes were successfully prepared using a surface-modification scheme followed with a metal adsorption-reduction procedure. The catalytic activities of these as-prepared catalysts were explored in

the solvent-free selective oxidation of benzyl alcohol using molecular oxygen. The catalytic results proved that the type and amount of functional group for functionalizing the TUD-1 support showed great impact on the catalytic performance. Amine-functionalized TUD-1 with an appropriate amount of amino group coverage displayed the best improvement owing to the enhanced metal-support interaction and finely tuned local surface basicity surrounding the Pd nanoparticles. Among all the catalysts, 1Pd/1.2APS-TUD exhibited a dramatically high q_{TOF} of $18\,571\text{ h}^{-1}$ for benzyl alcohol conversion. TUD-1 is superior to other mesoporous silicas due to its unique open 3-D sponge-like wide mesostructure which can effectively confine the nanoparticles and suppress the mass-diffusion resistance.

The particle size, morphology, structure and electron properties of metal nanoparticles may be varied by different preparation procedures, which subsequently impact the metal-support interaction and the catalytic performance. Therefore, Au-Pd bimetallic nanoparticles confined in SBA-15 mesoporous silica materials were successfully prepared by a novel Ar glow discharge plasma reduction following a conventional incipient-wetness impregnation method. Characterization and chemically probed reaction results suggests a Pd-rich shell/Au-rich core structure with abundant surface coordination-unsaturated Pd atoms for the effectively reduced AuPd/S15-p nanoparticles, which accounts for the extraordinary catalytic activity compared to Au and Pd monometallic catalysts for the selective oxidation of benzyl alcohol. As a green, rapid, efficient and safe reduction method, the plasma reduction outperforms the H_2 thermal reduction, showing uniform particle dispersion and size distribution, as well as superior catalytic performance, which is attributed to the nucleation and growth mechanism of plasma reduction

process. Further re-oxidation and reduction of plasma reduced Au-Pd catalyst result in the rearrangement of surface atoms, leading to an inferior catalytic performance.

7.2 *Future perspectives*

Based on the results of Chapter 5, finely tuned local surface basicity is suggested to enhance the dehydrogenation of benzyl alcohol which is the rate-controlling step during the reaction, suppress the formation of byproduct toluene, as well as facilitate the reactant adsorption and product desorption from the Pd active sites. However, only a limited number of characterization studies of noble metal based catalysts using *in-situ* techniques to apt to rationalize the metal-support interaction. During the past years, spectroelectrochemical methods, particularly X-ray absorption spectroscopy, have contributed to the understanding of the surface chemistry during the reaction, giving the real structure-activity and metal-support relationships. Therefore, more efforts would be delivered to unravel the surface reactions and their interconnectivity to gain a deeper knowledge of alcohol oxidation over noble metal catalysts.

During the oxidation of alcohols, oxygen is essential to give free active sites by oxidizing surface hydride to form water and removing surface impurities formed in side reactions. Since in most cases molecular oxygen cannot directly oxidize the substrates, the activation and transfer of oxygen is of great importance. Generally the activation of O_2 is suggested to occur on the defects or oxygen vacancies. In addition, the activated O_2 may exist in the form of lattice oxygen (O^{2-}) or other surface oxygen species such as chemisorbed oxygen O_2^- and O^- . For metal oxides support, O_2 may be readily activated on the defects of oxides and transferred via oxygen vacancies. Nonetheless, in this thesis, three different mesoporous silicas were employed as supports. Silica material itself is lack of oxygen defects or

vacancies. So the mechanism of O₂ activation and transfer is still ambiguous and obscure. Noble metal possesses the ability to activate O₂ while the oxygen-containing species (eg., -OH) of silicas may also serve as sites for O₂ activation. Therefore, further investigation is needed urgently to identify the mechanism of O₂ activation and transfer, whether on the metal surface or on the surface oxygen-containing groups and what is the state of O during the process.

Based on the results of Chapter 6, the particle nucleation and growth mechanism in the plasma reduction process is suggested to be different from H₂ thermal reduction, affording modified morphology and surface chemistry of metal nanoparticles and further oxidation and re-reduction of plasma reduced Au-Pd catalyst result in the atomic re-arrangement of nanoparticles, leading to an inferior catalytic performance. However, these results are indirect proofs. The catalyst obtained via plasma reduction may be unstable and undergo a subtle change once it is exposed in the air. Due to the limitation of experimental conditions, we cannot follow the *in-situ* plasma reduction process at this juncture at present. Hence, we attempt to build a set-up for catalyst preparation combined with *in-situ* characterizations which enable to obtain the real-time information of catalyst.

In this PhD work, mass transfer limitation is found to be inevitable over the mesoporous silicas based catalysts for the liquid-phase oxidation of alcohols. However, the mass transport resistance can be remarkably eliminated when the reaction is carried in gas-phase. Moreover, the convenient separation of catalysts from catalytic reaction and the practicability in industrial scale also encourage the study of gas-phase dehydrogenation of alcohols. Thus, it is desirable to develop new processes and catalysts for the conversion of benzyl alcohol to benzaldehyde in gas phase, particularly using solid catalysts with high selectivity and recyclability and

molecular oxygen as the oxidant. Further study would be conducted to optimize the processes under additive-free and mild conditions.

Appendix

A.1 Aerobic oxidation of benzyl alcohol over activated carbon supported manganese and vanadium catalysts: effect of surface oxygen-containing groups

Selective oxidation of alcohols to produce the corresponding aldehydes and ketones, in particular benzyl alcohol to benzaldehyde has been regarded as the essentially important organic transformations in synthetic chemistry. The corresponding carbonyl products have extensive applications in plastic, dyestuff, perfumery, flavor, pharmaceutical, and agro chemical manufactory [1-3]. From the viewpoints of environmentally benign process and atom economy, the liquid-phase selective oxidation of benzyl alcohol under mild conditions using air or molecular oxygen (aerobic oxidation) is preferable. A variety of noble metal catalysts, *e.g.*, Au/CeO₂ [4], Pd/HAP [5], and Au-Pd/TiO₂ [6] with superior activities have been developed for the aerobic oxidation of benzyl alcohols. In addition, highly efficient non-noble metal catalysts have also been reported recently in the same reaction [7-12]. Among various less-expensive transition metal catalysts, manganese and vanadium oxides have been widely engaged in the selective oxidations [8-9]. The catalytic activities of supported Mn and V catalysts are suggested to strongly depend on the nature of active centers, which can be specified as the dispersion, oxidation state, local symmetry environment, and metal-support interaction [13-17].

Activated carbon (AC) is extensively employed as a preferential catalyst support material due to its high surface area ($\sim 1000 \text{ m}^2/\text{g}$), tunable porosity (2~15 nm), and high stability in caustic and acidic conditions [18]. Both the texture and surface chemistry of AC support have distinct effect on the catalytic performance

of AC supported catalysts [19-20]. The variety and density of functional groups on the AC surfaces can be modified by suitable chemical or thermal treatments. In particular, oxidation of AC in gas or liquid phase is generally applied to form carboxyl, carbonyl, phenol, quinone and lactone groups on AC surfaces, leading to the increased surface oxygen density [21].

Oxygen-containing groups on the AC surface play a key role in both catalyst preparation and catalytic reactions. After pre-oxidization, AC surfaces change from hydrophobic to hydrophilic, which substantially increases the surface wettability and the interaction between AC support and the metal precursor in aqueous phase. Moreover, these polar surface oxygen groups remarkably influence the catalytic activity and selectivity by tuning the preferential reactant adsorption and product desorption. The surface oxygen effect has been extensively investigated in the selective hydrogenation of cinnamaldehyde [22-24]. The C=O bond of cinnamaldehyde favors interacting with the oxygen groups on support surfaces instead of the metal active sites, resulting in the poor activity and selectivity. Toebe *et al.* reported a 25-fold increment of the catalytic activity over a carbon nanofiber-supported platinum catalyst in the selective hydrogenation of cinnamaldehyde after removing the surface oxygen-containing groups [25]. Koningsberger and co-workers also suggested that the surface oxygen gave rise to the change in the electronic structure, thereby affect the catalytic activity of metal nanoparticles supported on carbon [26-28].

Our group has reported the characterizations of AC-supported manganese and vanadium catalysts and their applications in the aerobic selective oxidation of benzyl alcohol [8-10]. Effort was dedicated to understand the nature of catalytically active centers such as dispersion, oxidation state, local symmetry, and

the correlation between catalyst properties and the catalytic performances. Herein, in this chapter, we proceed to study the effect of the oxygen-containing groups on AC surfaces on the benzyl alcohol selective oxidation.

A.1.1 Experimental

A1.1.1 Catalyst preparation

Extra pure charcoal AC powder (Scharlau Chemie) was pretreated in an oxidative agent prior to loading metal precursors. In the liquid oxidation, pristine AC was treated via two different routes: (i) stirred in 10 M hydrogen peroxide (H_2O_2) at room temperature for 6 h and followed by washing with deionized water until the filtrate is free of peroxides [19]; (ii) refluxed in 0.5 M or 6 M nitric acid (HNO_3) at 413 K for 8 h followed by washing with deionized water until the filtrate is neutral. The ratio of liquid to AC powder was 30 mL of liquid to 1 g of AC [29]. After pretreatment, the samples were dried at 393 K under vacuum for 24 h. In the gas phase oxidation, pristine AC was annealed in a constant flow of 5 vol.% O_2/He at 698 K for 3 h [19]. The as-received AC support is donated as AC-pristine and the pre-oxidized AC supports are accordingly donated as AC-10M H_2O_2 , AC-0.5M HNO_3 , AC-6M HNO_3 and AC-3h O_2 .

The 5 wt.% Mn/C and 4 wt.% V/C catalysts were prepared by a conventional wet impregnation method [9] using manganese nitrate tetrahydrate (>97%) and ammonium metavanadate (99.8%) as precursors, respectively. In a typical preparation, a measured amount of metal precursor was added to 20 mL of deionized water preloaded with 1 g of AC, followed by vigorous stirring for 2 h and aging at room temperature for 12 h. The excess water was slowly evaporated in a water bath at 343 K under continuous stirring. The residues were further dried in a vacuum oven at 343 K overnight and annealed at 673 K for 3 h in a He flow of

30 mL min⁻¹. For V/C, the deionized water was replaced by an oxalic acid solution (2 M). The as-synthesized catalysts are donated as M/C-pristine, M/C-10M H₂O₂, M/C-0.5M HNO₃, M/C-6M HNO₃ and M/C-3h O₂ (M = Mn or V).

A.1.1.2 Catalyst characterization

Nitrogen physisorption, XRD, TEM measurements follow the description in section 3.1.1. FTIR measurement follows the procedure in section 3.1.2.

Cyclic voltammograms (CV) were measured in a 1 M KOH solution. The working electrode was prepared by dropping 20 μ L of the ink onto the glassy carbon electrode (GCE) surface. The ink was prepared by ultrasonically mixing 3 mg of AC support with 750 μ L of ethanol for 30 min, followed by adding 750 μ L of Nafion solution (0.05 wt.% in ethanol) and ultrasonically for another 30 min. Pt foil and Hg/HgO (1 M KOH) electrodes were used as counter and reference electrodes, respectively. All the potentials are given versus the Hg/HgO (1 M KOH) electrode. The potentials of CV test ranged between -0.8 and 0.3 V.

X-Ray absorption spectra (XAS) at Mn and V K-edges were measured at the X-ray demonstration and development beam line of the Singapore Synchrotron Light Source (SSLS) [30]. The samples were ground into fine powders and measured in the transmission mode under ambient conditions. The collected data were analyzed using the WinXAS 2.3 software package.

A.1.1.3 Catalytic reaction

The aerobic oxidation of benzyl alcohol with molecular O₂ was carried out in a bath-type reactor operated under atmospheric conditions. In a typical reaction run, 0.2 g of catalyst was loaded to a 50 mL glass flask pre-charged with 2.5 mmol of benzyl alcohol and 10 mL of toluene. The mixture was then heated to 373 K under vigorous magnetic stirring at 1000 rpm in order to exclude the external mass

transfer limitation [31]. Oxygen flow was bubbled at a flow rate of 10 mL min⁻¹ into the mixture to initiate the reaction. The reaction time was set as 4 and 2 h for Mn/C and V/C, respectively. After reaction, the solid catalyst was filtered off and the liquid products were analyzed using an Agilent gas chromatograph 6890 equipped with a HP-5 capillary column (30 m long and 0.32 mm in diameter, packed with silicabased supel cosil). Dodecane was the internal standard to calculate benzyl alcohol conversion and benzaldehyde selectivity [10].

A.1.2 Results and discussions

A.1.2.1 Catalytic results

The AC-supported catalysts, Mn/C and V/C, have been examined in the aerobic oxidation of benzyl alcohol in the presence of molecular oxygen, and the catalytic results are summarized in Figure A.1.1. Both Mn/C and V/C can effectively catalyze the reaction under mild conditions, producing benzaldehyde as the main product along with a trace amount of benzoic acid (less than 1%) as the byproduct. Pretreating AC in 10 M H₂O₂ elevates the conversion of benzyl alcohol from 31.7% to 42.0% over Mn/C and from 46.3% to 74.8% over V/C. Catalytic activity shows a remarkable enhancement after pretreating the AC support in oxygen flow and low concentration HNO₃ (0.5 M). Nevertheless, the benzyl alcohol conversion significantly decreases when pretreating the AC support in a 6 M HNO₃ solution. In summary, Mn/C shows the largest improvement of conversion from 31% to 67.3% under 0.5 M HNO₃ pretreatment of AC, whereas V/C exhibits the highest increment of catalytic activity from 46% to 92.6% of conversion under 3 h O₂ pretreatment of AC.

Figure A.1.1 Effect of pretreatment of AC on the catalytic properties and surface area of both Mn/C and V/C catalysts. Reaction conditions: catalyst, 0.2 g; benzyl alcohol, 2.5 mmol; O₂, 10 mL min⁻¹; temperature, 373 K; time, 4 h for Mn/C and 2 h for V/C.

A.1.2.2 Characterization results

A.1.2.2.1 Specific surface area

Catalyst surface area is considered as one of the most important factors controlling the catalytic performance. The specific surface areas for all the samples are depicted in Figure A.1.1. The surface areas of AC supports under various pretreatments are similar to that of pristine AC, showing a small and indistinct fluctuation, which is in accordance with a previous report that the oxidation under

mild conditions has no significant impact on the AC texture and structure [32]. Nevertheless, the pore walls of AC support are prone to collapse under drastic conditions, *e.g.*, concentrated acid [33]. A remarkable decline of surface area occurs when pretreating the AC support in concentrated HNO₃. The considerable deterioration of the benzyl alcohol conversion over both Mn/C-6M HNO₃ and V/C-6M HNO₃ is thus mainly attributed to the dramatic decrease of surface area. In summary, the variation of specific surface area is small for both Mn and V catalysts supported on the AC pretreated in 10 M H₂O₂, 0.5 M HNO₃ and 3 h O₂; the effect of surface area on the catalytic activity should be negligible.

A.1.2.2.2 Active sites

Figure A.1.2 shows the XRD patterns of Mn/C and V/C catalysts. All the catalysts only exhibit an intense and sharp diffraction peak at 26.6° ascribed to the (002) plane of carbon (PDF# 41-1478). No discernable peaks of manganese oxide and vanadium oxide are observed, suggesting that the formed MnO_x and VO_x nanoclusters are highly dispersed on AC support surfaces. The dispersion of nanoclusters was further investigated by TEM, and the results are illustrated in Figure A.1.3. All the catalysts show a similar dispersion, regardless of the pretreatment of AC support. The MnO_x and VO_x nanoclusters possess a uniform diameter of ca. 20 nm.

FigureA.1.2 XRD patterns of Mn/C (*upper*) and V/C catalysts (*lower*).

Figure A.1.3 TEM images of Mn/C (*left*) and V/C catalysts (*right*).

X-Ray absorption near-edge structures (XANES) was employed to study the

local structure and oxidation state of Mn and V active sites [34-35]. The normalized XANES spectra at Mn K-edge are illustrated in Figure A.1.4. All the Mn/C samples exhibit distinct and well-defined XANES features, in which the small pre-edge peak is assigned to $1s \rightarrow 3d$ transition. Mn supported on pristine AC and the AC pretreated in 10 M H_2O_2 , 0.5 M HNO_3 , and 3 h O_2 shows comparable pre-edge features, suggesting the similar local coordination structure of manganese sites. Nonetheless, manganese center possesses a different symmetry in Mn/C-6M HNO_3 due to the significant edge shift for this particular sample.

Figure A.1.4 Normalized Mn K-edge XANES spectra of Mn/C catalysts along with reference compounds.

These observations can be further quantitatively reflected from the edge energy shift and average valence listed in Table A.1.1. The average valences of Mn

in Mn/C-pristine, Mn/C-10M H₂O₂, Mn/C-0.5M HNO₃ and Mn/C-3 h O₂ are 2.79, 2.76, 2.73 and 2.70, respectively. All these values are close to that of Mn₃O₄ (2.67), implying the coexistence of Mn²⁺ and Mn³⁺ in these catalysts and a similar local coordination of Mn active sites comparable to that of Mn₃O₄ [10, 36-37]. The Mn species in Mn/C-6M HNO₃ shows a rather low valence of 2.42 which is in between the reference values of Mn₃O₄ and MnO, implying a dramatic change in the local symmetry of Mn coordination spheres and a lower content of Mn³⁺ as compared to other catalysts. More specifically, a conversion from Mn³⁺ to Mn²⁺ in the octahedral coordination occurs when Mn is supported on the AC pretreated in 6 M HNO₃.

Table A.1.1 X-ray absorption-main edge position and the average valence for Mn/C catalysts and reference compounds.

Sample	Edge position (eV) ^a	Valence
Mn/C	6547.1	2.79
Mn/C-10M H ₂ O ₂	6547.0	2.76
Mn/C-0.5M HNO ₃	6546.9	2.73
Mn/C-6M HNO ₃	6546.7	2.42
Mn/C-3h O ₂	6546.8	2.70
MnO	6544.0	2.00
Mn ₃ O ₄	6546.7	2.67
Mn ₂ O ₃	6548.5	3.00
MnO ₂	6551.9	4.00

^aTaken as the maximum of the first derivative of the K-edge spectrum with respect to the corresponding feature of Mn foil (6539.0 eV).

The local symmetry and oxidation state of vanadium supported on AC were also characterized using XANES. The normalized XANES spectra at V K-edge for V/C catalysts along with the reference vanadium compounds are shown in Figure A.1.5. All the spectra display a distinct pre-edge absorption feature contributed by the forbidden transition from 1s to 3d, which is predominately caused by mixing the 4p orbital of vanadium and 2p orbital of oxygen with the 3d orbital of

vanadium [38]. Almost identical spectra especially the pre-edge features for all the samples imply the similar electronic structure and site symmetries of vanadium centers.

Figure A.1.5 Comparison of normalized V K-edge XANES spectra for all types of V/C catalysts and reference compounds: (a) V foil; (b) V_2O_3 ; (c) V_2O_4 ; (d) V_2O_5 ; (e) PbV_2O_6 ; (f) NH_4VO_3 ; (g) Na_3VO_4 ; (h) V/C-pristine; (i) V/C-10M H_2O_2 ; (j) V/C-0.5M HNO_3 ; (k) V/C-6M HNO_3 ; (l) V/C-3h O_2 .

The quantitative XANES results are summarized in Table A.1.2 [38-39]. The pre-edge peak height and intensity are closely related to the local symmetry type, and can be employed to gain information on the coordination structure when comparing the spectrum with a known coordination environment. As shown in Table A.1.2, all the V/C catalysts show a slightly lower pre-edge peak height as compared to NH_4VO_3 (tetrahedral coordination). The samples were characterized

under ambient conditions, and moisture may decrease the pre-edge peak height. We conclude that the V/C samples possess a distorted tetrahedral coordination. The energy shift of pre-edge peak from main edge has been taken as a effective measurement for the oxidation state of vanadium [38]. As shown in Table A.1.2, the pre-edge energy shifts about 12.8 eV for tetrahedral vanadium (5+) species, 12.2 eV for octahedral vanadium (5+), and 11.0 eV for square pyramidal vanadium (5+). For V/C catalysts, the energy shift varies between 10.9 and 11.5 eV, suggesting the presence of vanadium under 5+ oxidation state.

As discussed in the above characterization results, Mn and V catalysts possess similar specific surface area, active site dispersion, local coordination structure and valence although the AC support is subjected to various mild oxidation pretreatments prior to the catalyst synthesis. Therefore, the effect of active site properties on the catalytic activity can be ruled out. Pretreating the AC support in concentrated HNO₃ significantly changes the nature of supported Mn active sites. The possible reason is that the active phase in a tetrahedral coordination is more stable than in an octahedral coordination; Mn³⁺ ions in distorted octahedral sites convert to Mn²⁺ in tetrahedral sites as reported in our previous study [9].

A.1.2.2.3 Surface oxygen

To measure the surface oxygen density, the electrochemical properties of AC support, subjected to different oxidation pretreatments, was examined in an alkaline solution, and the CV profiles are shown in Figure A.1.6. No distinct redox peaks are observed, implying the absence of quinone/hydroquinone groups on the AC surfaces [40]. It also reveals the electrochemical inactivity of the functional groups (under such circumstances) on the surface of pretreated-AC as suggested by Swiatkowski and co-workers [41]. The background of CV signal reflected from the

Table A.1.2 Energy positions of various spectral features in the V K-edge XANES spectra for V/C catalysts and reference compounds.

Sample	Pre-edge ^a (eV)	Main-edge ^{a, b} (eV)	E _{pre-edge} -E ₀ (eV)	E _{edge} -E _{pre-edge} (eV)	Pre-edge peak height (a.u.)	Pre-edge peak intensity ^c (a.u.)
V/C	5469.9	5481.4	4.9	11.5	0.41	1.50
V/C-10M H ₂ O ₂	5470.4	5481.6	5.4	11.2	0.39	1.37
V/C-0.5M HNO ₃	5470.4	5481.3	5.4	10.9	0.42	1.56
V/C-6M HNO ₃	5470.4	5481.4	5.4	11.0	0.41	1.51
V/C-3h O ₂	5470.4	5481.5	5.4	11.1	0.38	1.51
Na ₃ VO ₄	5469.9	5482.7	4.9	12.8	0.59	2.13
NH ₄ VO ₃	5470.4	5482.7	4.9	12.8	0.48	1.86
PbV ₂ O ₆	5470.4	5482.6	5.4	12.2	0.39	1.56
V ₂ O ₅	5470.4	5481.4	5.4	11.0	0.38	1.63
V ₂ O ₄	5470.4	5480.8	5.4	10.4	0.27	1.32
V ₂ O ₃	5470.4	5480.9	5.4	10.5	0.31	1.57

^aThe uncertainty in peak positions is estimated to be ± 0.2 eV.

^bMain-edge position is chosen as the midpoint of the absorption jump.

^cPeak intensity is calculated by peak height times width at half maximum.

area enclosed by the cyclic curve is related to the abundance of surface oxygen groups, *i.e.*, the higher the surface oxygen density on AC support, the larger the CV background and capacitance [42]. Figure A.1.6 verifies that pretreating the AC support in a mild oxidation environment greatly enlarges the CV background, suggesting the presence of the increased quantity of surface oxygen containing groups. Among these oxidation routes, gas phase pretreatment (in O₂ for 3 h) is the most effective to enhance the surface oxygen density [19]. Pretreating AC in 0.5 M HNO₃ exhibits better enrichment of oxygen-containing groups than in 10 M H₂O₂, which is probably due to the over-oxidation of surface oxygen groups in concentrated H₂O₂. AC support pretreated in 6 M HNO₃ displays an extraordinarily small CV background. Similar result has been reported for carbon black: HNO₃ pretreated carbon black shows a larger enclosed area of CV than as-received carbon black due to the increased surface oxygen groups, whereas further prolonging the pretreatment time or raising the HNO₃ concentration displays a shrunk background area due to the elimination of surface oxygen by over-oxidation [40].

Figure A.1.6 Cyclic voltammograms (CVs) on AC supports with different pretreatments in 1 M KOH solution with a scan rate of 50 mV s^{-1} .

The surface oxygen groups on AC support were also identified by FTIR, as illustrated in Figure A.1.7. Three major absorbencies centered at 1750 , 1530 , and 1230 cm^{-1} can be discerned, which have been assigned to the C=O stretching of carboxylic groups, carboxylic groups or an aromatic ring-stretching mode, and the C-O stretching of ethers, lactones, phenol or carboxylic anhydrides, respectively [19, 43]. These absorbencies are remarkably enhanced after pretreating the pristine AC support, suggesting that the AC support surface is covered by various oxygen-containing groups after oxidation. The intensity of the doublet centered at 2347 cm^{-1} , assignable to the hydrogen-bonded hydroxyl groups [43] also

remarkably increases especially for the AC support pretreated in 3 h O₂, implying the preferential formation of hydroxyl groups in gas-phase oxidation. The AC support pretreated in 6 M HNO₃ shows a distinct spectrum. The intensities of 1750 and 1230 cm⁻¹ bands increase dramatically and the band at 1530 cm⁻¹ shifts to 1580 cm⁻¹. Moreover, a weak overlap at 1850 cm⁻¹ is discernable, which is contributed by cyclic anhydrides or lactones. All these variations can be attributed to the low density of oxygen-containing groups on strongly acidified AC surfaces after pretreating the AC in concentrated HNO₃. In summary, oxidizing AC support can create a substantial amount of oxygen-containing groups on the support surfaces; gas-phase oxidation predominately introduces hydroxyl and carbonyl groups whereas liquid-phase oxidation facilitates the formation of highly acidic surface oxygen groups.

Figure A.1.7 FTIR spectra of various AC supports: (a) AC-pristine; (b) AC-10M H₂O₂; (c) AC-0.5M HNO₃; (d) AC-6M HNO₃; (e) AC-3h O₂.

A.1.2.3 Discussions

Both CV and FTIR characterizations prove that different pre-oxidation routes

result in different surface properties of AC support: gas phase oxidation mainly increases the concentration of neutral or mildly acidic surface hydroxyl and carbonyl groups while oxidation in the liquid phase forms strongly acidic carboxylic anhydrides and lactones especially the carboxylic acids, as also reported by Figueiredo *et al.* [19]. Consequently, the effect of surface oxygen on the catalytic performance can be identified in terms of the variety and density of surface oxygen-containing groups due to the fact that specific surface area, dispersion and nature of active sites do not substantially change after pretreating the AC support. It is clearly shown that the catalytic activity is correlated to that of the surface oxygen density, which suggests the abundance of surface oxygen is favorable for enhancing the catalytic oxidation. These surface oxygen groups change the AC support surface from hydrophobic to hydrophilic and from non-polar to polar, which facilitates the preferential adsorption of benzyl alcohol and the subsequent desorption of the hydrophobic product benzaldehyde. In addition, the interaction between active sites and AC support is remarkably strengthened, which is due to the strong anchoring effect of these surface oxygen complexes and the promoted electron transfer between the support, the active centers and the reactant. This leads to the enhancement in the hydrogen abstraction from -OH group, which is proposed as the rate-limiting step for the selective oxidation of benzyl alcohol. Noticeably, Mn/C shows the highest conversion when the AC support is pretreated in diluted HNO₃ (Mn/C-0.5M HNO₃), whereas V/C exhibits the best catalytic activity after pretreating the AC support in gas phase (V/C-3h O₂). A possible explanation to this inconsistency is that different varieties of surface oxygen groups favor the adsorption of different metal precursors during the catalyst preparation. Romanmartinez *et al.* have rationalized that the acidic or

basic properties of support and metal precursor solution strongly influence the interaction between metal precursors and support surfaces [44]. The interaction of cations with support is favored when the precursor solution is more basic than the aqueous slurry of support [45]. For Mn/C catalysts, the precursor solution of $\text{Mn}(\text{NO}_3)_2$ is neutral, which is more basic than the aqueous slurry of pretreated AC support. Therefore, the interaction of Mn^{2+} is favored on 0.5 M HNO_3 treated AC surfaces, which has more carboxylic acid groups. For V/C catalysts, the basic precursor solution of NH_4VO_3 is prone to interact with AC surfaces pretreated in 3 h O_2 , which has more hydroxyl and carbonyl groups and less acidity. Hence, as discussed above, both the variety and the density of the surface oxygen groups are critical to the catalytic performance during the selective oxidation of benzyl alcohol.

A.1.3 Conclusions

In this chapter, manganese oxide and vanadium oxide supported on AC catalysts were synthesized by a conventional wet-impregnation method. Both liquid and gas phase oxidation pretreatments of AC support enhanced the catalytic activity in the aerobic selective oxidation of benzyl alcohol. Benzyl alcohol conversion was remarkably improved from 31% to 67% over Mn/C-0.5M HNO_3 and V/C-3h O_2 exhibited a significant enhancement of conversion from 46% to 93%. XRD and TEM verified the similar dispersion of catalytically active sites regardless of pretreating the AC support. XANES revealed that the nature of catalytic species, *e.g.*, local coordination environment and oxidation state of both Mn/C and V/C catalysts remained unchanged before and after pretreating the AC support via different oxidation routes. Therefore, the improved catalytic performance can be attributed to both the specific variety and the increased density

of the oxygen-containing complexes on AC support surfaces, which has been verified using CV and FTIR. This work has been published in Catalysis Letters (Chen *et al.* Catalysis Letters, 2011, 141 (1), 149-157); reuse in this chapter is under the permission of Springer Science+Business Media.

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A.2 Pd catalysts supported on MnCeO_x mixed oxides and their catalytic application in solvent-free aerobic oxidation of benzyl alcohol: support composition and structure sensitivity

Among various transition metal and rare earth mixed oxide catalysts, MnCeO_x has attracted a great attention because of its potential industrial applications due to its high activity and versatility in many catalytic reactions, such as the catalytic wet oxidation (CWO) of waste waters containing phenol [1], ammonia [2], and pyridine [3], the combustion of volatile organic compounds (VOCs) [4], and the conversion/decomposition of NO_x [5-6]. The superior activities of MnCeO_x compared to pure MnO_x and CeO₂ oxides are attributed to the synergistic interactions between manganese and cerium oxides. The MnO_x domain with high dispersion and multiple oxidation states serves as the main active site, while CeO₂ acts as a promoter to enhance the oxygen mobility due to its unique capacity of storing oxygen under oxidizing conditions and releasing oxygen under reducing conditions. This is achieved through the transformation between Ce⁴⁺ and Ce³⁺ oxidation states, forming abundant surface and bulk vacancies to improve the redox capabilities [7-9].

A large number of previous studies have demonstrated that the catalytic activity of MnCeO_x composites strongly depends on the compositions, and the textural, structural and redox properties of these materials [1, 10-11]. Several preparation routes have been developed to obtain MnCeO_x with controlled physicochemical properties Co-precipitation [12] and redox-precipitation [7] are commonly employed to prepare crystalline and amorphous materials, respectively. The phase segregation of oxide domains correlates with the Mn/Ce molar ratio and the preparation method [13]. Due to the different precipitation kinetics of metal

precursors, co-precipitation method results in segregated manganese and cerium oxide crystallites with surface-enriched Ce. More specifically, either a thin layer of Ce-rich oxide covering the Mn crystallites or the co-existence of large MnO_x crystallites and small aggregates of Mn/Ce solid solution seems to be formed [14]. In contrast, redox-precipitation route favors the simultaneous precipitation of MnO_x and CeO_2 , thus leading to a homogeneous mixture at atomic level of Mn and Ce oxide species [15]. Our group has synthesized a series of amorphous MnCeO_x by redox-precipitation method, which has been tested in the catalytic aerobic oxidation of benzyl alcohol [16]. This work demonstrated that MnO_x is the active component and the addition of highly dispersed CeO_2 promotes the catalytic performance by enhancing the redox properties of MnCeO_x .

Nonetheless, a rapid loss of catalytic activity was found over MnCeO_x materials in most cases, which is mainly attributed to either the deposition of carbonaceous by-products on the catalyst surface or the leaching of the active metals during the reaction. This activity loss can be suppressed by adding a promoter. Santiago *et al.* reported that doping the MnCeO_x mixed oxides with a certain amount of potassium showed an improved performance and stability of the catalyst since K^+ could act as a modifier or chemical promoter [17]. Hamoudi *et al.* suggested that the catalyst deactivation could be diminished by a three-component-catalyst using noble metals promoters, *e.g.*, Ag and Pt, to significantly reduce the amount of carbonaceous deposits, prolonging the catalyst life [18]. Tang *et al.* studied the effect of Ag addition to MnCeO_x on the complete oxidation of formaldehyde and suggested that the enhanced activity was due to the improved oxygen activation on the catalyst surfaces and the oxygen mobility among Ag, Mn, and Ce [12]. Ru catalysts supported on MnCeO_x were also

reported to be highly active for alcohol oxidations reactions [19-20]. Recently, Zou *et al.* have shown that a Pd/MnO_x-CeO₂ catalyst synthesized by a surfactant-assisted precipitation method exhibits excellent activity in CO oxidation due to the accelerated oxygen activation in gas-phase and the oxygen transfer via spillover [21].

In this chapter, we prepared both crystalline and amorphous MnCeO_x supports. Pd particles were immobilized on these mixed oxides by a facile microwave-assisted polyol reduction (MAPR) method. The catalytic performance was evaluated in the selective oxidation of benzyl alcohol using molecular oxygen under solvent-free conditions. Benzyl alcohol oxidation was selected as probe reaction due to not only its relatively high reactivity but also the limited numbers of possible by-products. Various physicochemical characterization techniques were employed to investigate the textural, structural and redox properties as well as the surface composition of these Pd/MnCeO_x catalysts. The catalytic performance was correlated with these properties in a comparative manner between amorphous and crystalline support materials.

A.2.1 Experimental

A.2.1.1 Catalyst synthesis

Crystalline MnCeO_x supports with different Mn/Ce molar ratios (1:3, 7:3, and 10:1) were synthesized following a well-established co-precipitation procedure [8]: 100 mL of a solution of Mn(NO₃)₂·4H₂O and Ce(NO₃)₃·6H₂O with a total concentration of 150 g/L and a given nominal Mn/Ce mole ratio was prepared. A 2 M NaOH aqueous solution was added drop wise at 323 K under vigorous stirring until the pH value was 10.5. The precipitate was further aged at 323 K for 2 h. The obtained solid was filtrated, washed with deionized water, dried at 373 K for 12 h,

and calcined at 773 K for 6 h in air. The as-calcined MnCeO_x support was designed as $x\text{MnyCe-C}$, being x/y the nominal molar ratio of Mn/Ce. The amorphous MnCeO_x supports were prepared by redox-precipitation [15]: A certain amount of KMnO_4 precursor dissolved in deionized water was titrated with an aqueous solution containing both $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ at 343 K under vigorous stirring, where KMnO_4 was in a 10% stoichiometric excess. A 2 M NaOH aqueous solution was added drop wise to maintain a constant pH value at 8.0. After further stirring for 1 h, the obtained solid was filtrated, repeatedly washed with hot deionized water, dried at 373 K for 12 h, and calcined in air at 673 K for 6 h. This support was denoted as $x\text{MnyCe-A}$. For comparison, pure manganese oxide (MnO_x) and cerium oxide (CeO_2) were also prepared by co-precipitation using $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as precursors, respectively.

Palladium nanoparticles supported on these calcined MnCeO_x mixed oxides were successfully prepared by a facile MAPR procedure as reported by Guo *et al.* [22]. To deposit Pd precursors onto MnCeO_x mixed oxides, 0.1 g of support was immersed in 94.0 μL of PdCl_2 aqueous solution (0.05 M) and dried at 373 K in vacuum. The obtained solid was added to ethylene glycol (EG, 40 mL) and sonicated for 30 min to produce 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 433 K in 0.5 min and kept at the same temperature for another 1.5 min. After cooling to room temperature, the solid was filtrated, washed with deionized water and dried at 373 K in vacuum. The as-synthesized catalyst was denoted as $\text{Pd}/x\text{MnyCe-M}$ ($M = \text{C}$ or A for crystalline or amorphous structure,

respectively).

A.2.1.2 Catalyst characterizations

Nitrogen physisorption, XRD, TEM, ICP and XPS measurements follow the description in section 3.1.2.

Hydrogen temperature-programmed reduction (H_2 -TPR) and oxygen temperature-programmed desorption (O_2 -TPD) measurements were carried out using an Autosorb-1C system (Quanta Chrome), equipped with a thermal conductivity detector (TCD). Prior to each H_2 -TPR run, 100 mg of the sample was loaded in the quartz tube and pretreated with ultra-pure air at 373 K for 3 h. After cooling to room temperature, the gas flow was switched to 5 vol.% H_2/Ar and the base line was monitored until it became stable. The sample cell was heated at a ramping rate of 5 K min^{-1} and held at 873 K for 1 h to ensure the complete reduction. For the O_2 -TPD test, 100 mg of the sample was pretreated in pure O_2 at 823 K for 1 h. After cooling to room temperature, the sample was flushed with pure helium until the base line became stable. The desorption was conducted by heating the sample to 1173 K with a heating rate of 10 K min^{-1} .

A.2.1.3 Catalytic activity

The catalytic evaluation follows the procedure in section 3.3.

A.2.2 Results and discussion

A.2.2.1 Catalytic results

Both crystalline and amorphous MnCeO_x supported Pd catalysts have been tested in the selective oxidation of benzyl alcohol in presence of molecular oxygen. The results are listed in Table A.2.1. 0.5 wt. % Pd can be deposited on MnO_x support while only 0.36 wt.% on CeO_2 . In addition, the Pd loading increases with the addition of Mn to Ce. Therefore, mixing Mn with Ce to form MnCeO_x mixed

oxides leads to an enhanced Pd deposition. Resulting in more catalytic active sites. Despite of a 23.4% conversion of benzyl alcohol, Pd/CeO₂ shows a 88.9% selectivity towards benzaldehyde due to the formation of a large amount of toluene as undesired by-product. Pd/MnO_x exhibits a poor catalytic conversion of 17.9% along with a 99.4% benzaldehyde selectivity. Regardless of the support structure and composition, either benzyl alcohol conversion or selectivity towards benzaldehyde can be enhanced using MnCeO_x mixed oxides supports. The benzaldehyde selectivity is well maintained above 98% whereas the catalytic activity depends on the nature and composition of support materials. For Pd catalyst supported on both MnCeO_x-C and MnCeO_x-A materials, the catalytic activity (*q*TOF) first increases after adding small amount of Mn to Ce up to a maximum value, and then slightly decreases with further addition. The highest *q*TOFs are achieved over Pd/7Mn3Ce-C (15 325 h⁻¹) and Pd/7Mn3Ce-A (14 438 h⁻¹) for MnCeO_x crystalline and amorphous support materials, respectively. A control reaction was also carried out over a physical mixture of Pd/CeO₂ and Pd/MnO_x catalyst. A poor conversion of 9.6% is obtained, indicating that only chemically mixed Mn and Ce species can facilitate the catalytic reaction. In addition, bare supports show negligible catalytic activity (entries 10-11), implying that Pd acts as the sole active species. Therefore, the improved catalytic activity on Mn-Ce mixed oxides could be correlated with the synergetic interactions among Pd, CeO₂ and MnO_x domains. As a structural and electronic promoter, CeO₂ improves the oxygen storage and release ability, enhances the oxygen mobility and availability, and tunes the redox properties of the mixed oxides when associated with MnO_x [16].

Table A.2.1 Catalytic performances of 0.5 wt.% Pd containing catalysts supported on MnCeO_x^a.

Entry	Catalyst	Pd content ^b (wt.%)	Conv. (%)	Select. (%)			<i>q</i> TOF ^c (h ⁻¹)
				benzal dehyde	tolu ene	benzoi c acid	
1	Pd/CeO ₂	0.36	23.4	88.9	11.1	0	17572
2	Pd/1Mn3Ce-C	0.28	15.6	99.1	0.9	0	14850
3	Pd/7Mn3Ce-C	0.32	18.4	98.6	0.4	0	15325
4	Pd/10Mn1Ce-C	0.41	23.2	98.7	0.8	0.5	15066
5	Pd/1Mn3Ce-A	0.27	12.3	98.3	1.2	0.4	12085
6	Pd/7Mn3Ce-A	0.38	20.6	99.3	0.7	0	14438
7	Pd/10Mn1Ce-A	0.51	15.6	99.0	1.0	0	8688
8	Pd/MnO _x	0.5	17.9	99.4	0.6	0	9526
9	Pd/CeO ₂ +Pd/MnO _x ^d	0.41	9.6	100	0	0	6246
10	10Mn1Ce-C	-	1.0	100	0	0	-
11	7Mn3Ce-A	-	0.9	100	0	0	-
12	Pd/7Mn3Ce-C ^e	0.32	0.9	97.9	2.1	0	777
13	Pd/7Mn3Ce-A ^e	0.38	0.9	99	1	0	605

^a reaction conditions: catalyst, 20 mg; benzyl alcohol, 50 mmol; O₂, 20 mL/min; temperature, 433 K; reaction time, 1 h; Carbon balance, 98.5%.

^b Pd content was tested by ICP.

^c *q*TOF is calculated by using the Pd content obtained from ICP.

^d physical mixture of Pd/CeO₂ and Pd/MnO_x catalyst (1:1 mass ratio).

^e N₂ used instead of O₂.

The evolution of the catalytic performance as a function of time was studied over Pd/7Mn3Ce-C and Pd/7Mn3Ce-A catalysts. The results are depicted in Figure A.2.1. The conversion of benzyl alcohol increases monotonously with the reaction time, whereas the *q*TOF decreases. The selectivity toward benzaldehyde is high (≥97%) over both catalysts during the first 0.5 h of reaction. Nevertheless, it gradually deteriorates at longer reaction time, which is ascribed to the formation of benzoic acid by further oxidation of benzaldehyde. The benzyl alcohol conversion over Pd/7Mn3Ce-C reaches a plateau after 4 h while that of Pd/7Mn3Ce-A increases continuously, implying a faster deactivation for Pd/7Mn3Ce-C which may be attributed to the pronounced deposition of carbonaceous species [19]. After 10 h, 63.1% and 81.9% conversion of benzyl alcohol are obtained over

Pd/7Mn3Ce-C and Pd/7Mn3Ce-A catalysts, respectively.

Figure A.2.1 Time courses of Pd/7Mn3Ce-C and Pd/7Mn3Ce-A for benzyl alcohol oxidation. Reaction conditions: catalyst, 20 mg; benzyl alcohol, 50 mmol; O₂, 20 mL min⁻¹; temperature, 433 K.

A.2.2.2 Catalyst characterizations

Table A.2.2 summarizes the textural properties of all synthesized MnCeO_x support materials as well as MnO_x and CeO₂. Crystalline MnO_x possesses a rather low surface area of 36.3 m² g⁻¹. The specific surface area increases to 48.0 m² g⁻¹ upon adding Ce and monotonously increases with further Ce addition. 1Mn3Ce-C shows a specific surface area of 116.0 m² g⁻¹ which is higher than that of CeO₂. The increased surface area after adding Ce to MnO_x implies a close interaction

between MnO_x and CeO_2 . Similar to the crystalline counterparts, an increase of Ce content also gradually increases the surface area for MnCeO_x -A samples, being 1Mn3Ce-A sample the one that possesses the largest surface area ($217.6 \text{ m}^2 \text{ g}^{-1}$). In general, the pore volumes of all MnCeO_x samples are larger than those of pure MnO_x and CeO_2 . Amorphous MnCeO_x support materials exhibit larger surface areas but smaller pore diameters compared to crystalline MnCeO_x samples, implying that the crystal-growth of MnCeO_x -C can be suppressed more significantly during the redox reaction among Mn^{2+} , Ce^{3+} , and MnO_4^- [23].

Table A.2.2 Textural and structural properties of MnCeO_x support materials with different Mn/Ce molar ratios.

Entry	Sample	Molar ratio (Mn/Ce)	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)	Grain size (nm)	Lattice constant (nm)
1	CeO_2	0:1	79.4	0.19	9.1	13.3	0.5416^a
2	1Mn3Ce-C	1:3	116.0	0.32	13.4	5.0	0.5279^a
3	7Mn3Ce-C	7:3	67.6	0.38	15.7	5.3	0.5318^a
4	10Mn1Ce-C	10:1	48.0	0.36	24.9	8.4	0.5376^a
5	1Mn3Ce-A	1:3	217.6	0.46	9.0	-	-
6	7Mn3Ce-A	7:3	190.6	0.47	1.8	-	-
7	10Mn1Ce-A	10:1	101.5	0.32	3.6	-	-
8	MnO_x	1:0	36.3	0.33	36.4	38.3	0.9362^b

^a grain size and lattice constant were calculated according to CeO_2 (111) peak.

^b grain size and lattice constant were calculated according to Mn_2O_3 (Bixbyite-C) (222) peak.

Figure A.2.2 shows the XRD patterns of MnCeO_x supports along with the catalysts containing 0.5 wt.% Pd. The calculated average grain sizes of CeO_2 and MnO_x and the lattice constants (only for crystalline samples) are listed in Table A.2.2. Pure MnO_x exhibits the characteristic diffraction peaks ascribed to Mn_2O_3 (Bixbyite-C, PDF# 41-1442) and Mn_3O_4 (Hausmannite, PDF# 24-0734), suggesting the co-existence of +2 and +3 oxidation states of Mn. The XRD pattern

of pure cerium oxide shows intense and sharp peaks at $2\theta = 28.5^\circ$, 33.1° , 47.5° and 56.3° which can be assigned to CeO_2 (PDF# 43-1002). For 1Mn3Ce-C sample, no other crystalline phase but broad reflections due to cubic fluorite structure of CeO_2 are observed, which could be attributed to the formation of solid solution between manganese and cerium oxides by incorporating Mn cations into CeO_2 lattices. For 7Mn3Ce-C and 10Mn1Ce-C samples, in addition to the broad reflection peaks of CeO_2 , diffraction peaks ascribed to Mn_2O_3 and Mn_3O_4 appear, suggesting the co-existence of segregated Mn and Ce oxide phases. The remarkable weakening and broadening of these diffraction peaks with increasing Ce content suggest that the incorporated cerium enhances the dispersions for both Ce and Mn species [24]. Furthermore, several weak diffraction peaks that fit the d -spacing of MnO_2 (Ramsdellite, PDF# 39-0375) and Mn_5O_8 (PDF# 39-1218) are also observed, implying that Ce addition might increase the oxidation state of Mn and stabilize Mn oxide species in higher oxidation states. These results are consistent with a recent report indicating that the phase composition of crystalline MnCeO_x strongly depends on the molar ratio of Mn/Ce [25].

Figure A.2.2 XRD patterns of MnCeO_x supports along with the 0.5 wt.% Pd catalysts containing: (a) crystalline; (b) amorphous.

Noteworthy, the diffraction peaks attributed to the fluorite-like structure of CeO₂ shift toward higher Bragg angles in the presence of more Mn, implying the contraction of CeO₂ unit cell. This is further confirmed by the changes of lattice constants of MnCeO_x-C samples, as depicted in Table A.2.2. All the calculated lattice constants monotonously increase with increasing the Mn content. Nevertheless, all constants are smaller than those of both pure CeO₂ (0.5146 nm) and MnO_x (0.9362 nm). Considering the smaller ionic radius of Mn²⁺ (0.065 nm) and Mn³⁺ (0.066 nm) compared to that of Ce⁴⁺ (0.094 nm), the small lattice constants for MnCeO_x-C suggest that Mn ions may be incorporated into the ceria

lattice, provoking the unit cell contraction. This suggests the formation of manganese-cerium oxides solid solutions. Furthermore, the diffractions peaks of CeO_2 broaden after Mn addition, indicating that crystal-growth and concomitant sintering are suppressed. Thus, small crystallites with a more defective lattice and less crystalline character are formed.

Amorphous MnCeO_x -A samples exhibit significantly different XRD patterns compared to MnCeO_x -C. A broad peak spanned in the 2θ range of $20\text{--}38^\circ$ along with other less intense peak in the range of $40\text{--}60^\circ$ suggest the lack of long-range order, which may be due to the hindered growth of large crystalline domains during redox-precipitation since Mn and Ce are intimately contacted [23]. A decrease of peak intensity with increasing Mn/Ce ratio implies that these diffractions are mainly associated with ceria species [15]. No reflections due to Pd can be observed after depositing Pd on both 7Mn3Ce-C and 7Mn3Ce-A supports, indicating the highly dispersed nature of these supported Pd nanoparticles.

Figure A.2.3 shows TEM images of Pd/7Mn3Ce-C, Pd/7Mn3Ce-A as well as Pd/ CeO_2 and Pd/ MnO_x . All these catalysts, except amorphous Pd/7Mn3Ce-A, consist of a large number of nanocrystallites of metal oxide grains. According to the size and morphology, two kinds of particles can be distinguished for Pd/ MnO_x catalyst: round-large and nonfaceted crystals with a size of ca. 40 nm and small aggregates (<7 nm) which are attributed to Mn_2O_3 and Mn_3O_4 . For Pd/7Mn3Ce-C catalyst, a new crystal phase besides Mn_2O_3 and Mn_3O_4 can be discerned which exhibits rod-like shape with a length ranging from several nanometers to several micrometers. These nanorods were also observed by Perez-Omil *et al.* and attributed to MnO_2 [26]. Pd/7Mn3Ce-A only exhibits a densely packed amorphous matrix. The CeO_2 nanocrystallites are of ca. 15 and 8 nm for Pd/ CeO_2 and

Pd/7Mn3Ce-C respectively, in good agreement with the grain sizes derived from XRD (listed in Table 2). This further confirms that adding a small amount of Ce not only increases the surface area of MnO_x but also enhances the dispersions for both Ce and Mn species [24]. Therefore, the Mn and Ce oxide phases in Pd/MnCeO_x-A are homogeneously mixed at quasi-molecular level, forming a prevalently amorphous structure [13], whereas in Pd/MnCeO_x-C sample, they mostly retain the typical features of MnO_x crystallites. Pd nanoclusters with small sizes and high dispersion can be seen on the support surfaces. On Pd/7Mn3Ce-A, only the sporadic presence of Pd nanoparticles is observed, implying that Pd species may be embedded in the irregular and amorphous matrix.

Figure A.2.3 TEM images of representative MnCeO_x supported Pd catalysts.

H_2 -TPR profiles of representative MnCeO_x support materials are illustrated in Figure A.2.4. Pure MnO_x shows two main reduction peaks (327 and 452 °C),

which are ascribed to a two-step reduction: reduction of MnO_2 and/or Mn_2O_3 to Mn_3O_4 and the subsequent reduction of Mn_3O_4 to MnO [27]. Pure CeO_2 shows a broad and indistinct reduction peak starting from 300 °C with a maximum at 380 °C, which is assigned to the easily reducible Ce^{4+} species [1, 16]. When mixing Mn with Ce to form crystalline 7Mn3Ce-C, the two-step Mn reduction is retained. However, these two characteristic reduction peaks shift to lower temperatures, 287 and 393 °C, respectively, indicating an improved reducibility and oxygen mobility caused by the incorporation of Ce as well as the interaction between manganese and cerium oxides [1, 12]. The increased ratio of first-to-second peak area for 10Mn1Ce-C compared to MnO_x qualitatively reveals the existence of a larger fraction of manganese oxide species having higher oxidation states. To study the possible effect of bulk Mn/Ce composition, the reducibility of 10Mn1Ce-C was also examined as depicted in Figure A.2.4. 10Mn1Ce-C sample gives similar TPR profile to that of 7Mn3Ce-C, though both reduction peaks of Mn slightly shift to higher temperatures, further confirming the enhanced reducibility provided by incorporating Ce.

The reduction of amorphous 7Mn3Ce-A shows a different pattern, exhibiting two poorly resolved peaks at 327 and 363 °C, respectively. In fact, these two overlapped peaks can be assigned to the reduction of isolated Mn^{4+} [15] and Mn^{3+} species due to the absence of reduction at around 450 °C. The remarkable shift towards lower temperature is contributed by three factors: molecular-level Mn-Ce inter-dispersion, higher average oxidation states, and a strong Mn-O-Ce interaction [13]. The reduction is promoted by highly coordinately unsaturated Mn species and, perhaps, the presence of neighboring Ce^{4+} ions, which undergo reduction to Ce^{3+} species. The TPR results reveal that the mobility and availability of lattice oxygen

are enhanced due to the incorporation of Ce and the strong synergistic interaction between Mn and Ce oxides. CeO₂, well-known for its oxygen storage capacity, can provide oxygen to Mn, thereby increasing its oxidation state. Manganese species possess higher oxidation states (+3 and +4) and enhanced reducibility in amorphous MnCeO_x than those in crystalline counterpart (+2, +3 and +4).

Figure A.2.4 H₂-TPR profiles of representative MnCeO_x support materials.

TPD tests, an effective method to examine the mobility of oxygen species, were performed on three representative catalysts: Pd/7Mn3Ce-A, Pd/7Mn3Ce-C and Pd/10Mn1Ce-C. The results are shown in Figure A.2.5. The indistinct and broad peak at 260 °C is assigned to the surface active oxygen species, probably chemisorbed oxygen O₂⁻, which are originated from the oxygen vacancies on the interface of MnO_x and CeO₂ during the oxidation pretreatment before TPD test [21]. This peak is more intense in Pd/7Mn3Ce-A than in Pd/7Mn3Ce-C, indicating

larger abundance of O_2^- component over Pd/7Mn3Ce-A. Nonetheless, this peak nearly disappears in Pd/10Mn1Ce-C, implying the lack of such interface oxygen species, probably due to the decrease of Mn-Ce interface as a result of discrete contact among large MnO_x and CeO_2 crystallites. The peak at ca. 630 °C, which is attributed to the chemisorbed atomic oxygen O^- , is significantly intense in Pd/7Mn3Ce-C and Pd/10Mn1Ce-C while it becomes a shoulder in the Pd/7Mn3Ce-A. The broad peak centered at 750 °C in both Pd/7Mn3Ce-C and Pd/10Mn1Ce-C samples is assigned to the lattice oxygen O^{2-} . However, this peak drastically shifts to 692 °C in Pd/7Mn3Ce-A sample, indicating the remarkably enhanced oxygen mobility.

Figure A.2.5 O_2 -TPD profiles of representative Pd/MnCeO_x catalysts.

XPS is a useful technique to analyze phenomena occurring at the outermost layers of MnCeO_x surfaces and evaluate the surface species (Ce, Mn, O and Pd) in

non-stoichiometric surface oxides of both crystalline and amorphous MnCeO_x supports and their corresponding Pd-containing catalysts. To understand the effect of support structure and Pd deposition on the surface chemistry, we have examined 7Mn3Ce-C and 7Mn3Ce-A supports and their corresponding Pd-containing catalysts. The evolution of XPS spectra of Ce 3d, Mn 2p, O 1s and Pd 3d core levels are shown in Figure A.2.6 and the surface compositions are summarized in Table A.2.3. 7Mn3Ce-A exhibits a Mn/Ce ratio (2.13), which is close to the theoretical bulk composition, indicating a homogeneous dispersion of Mn and Ce species due to the simultaneous co-precipitation. Whereas 7Mn3Ce-C gives a slightly lower Mn/Ce atomic ratio (1.96), suggesting that crystalline support is surface-enriched in Ce. This Ce surface-enrichment of co-precipitated MnCeO_x can be attributed either to a partial coverage of Mn crystals by a thin layers of Ce-rich oxide or to the presence of large MnO_x crystals which contributes less significantly to the total surface area than small Ce-rich Mn-Ce solid solution crystallites [14]. After adding Pd, Mn/Ce ratio remains almost unchanged for Pd/7Mn3Ce-A (2.19) while decreases for Pd/7Mn3Ce-C (1.73), implying that Pd is uniformly dispersed in Pd/7Mn3Ce-A while exhibits a preferential anchoring on Mn species in Pd/7Mn3Ce-C. In amorphous samples, the relative abundance of both Mn and Ce are higher than those in crystalline samples, further verifying the good inter-dispersion of Mn and Ce species in amorphous MnCeO_x . Pd/7Mn3Ce-C shows a slightly higher surface Pd concentration (0.48%) compared to Pd/7Mn3Ce-A (0.31%), suggesting that more exposed Pd active sites are available on Pd/7Mn3Ce-C sample, while Pd may be partially embedded or covered in Pd/7Mn3Ce-A. Trovarelli *et al.* also reported that precious metals such as Pt and Pd interact strongly with CeO_2 and tend to penetrate inside it [9].

The Ce 3d core level spectra in Figure A.2.6a were deconvoluted using two spin-orbit components (u and v refer to the $3d_{3/2}$ and $3d_{5/2}$ spin-orbit components, respectively) to distinguish Ce^{3+} and Ce^{4+} contributions. The spectra of Ce^{4+} can be resolved into six features (u , u'' , u''' , v , v'' , and v''') while Ce^{3+} can be fitted with two features (u' and v') [21]. The high BE doublet u'''/v''' at 916.9 and 898.5 eV is assigned to the final state of $\text{Ce}^{4+} 3d^9 4f^0 \text{ O } 2p^6$. The doublet u''/v'' at 907.3 and 888.5 eV is attributed to the hybridization state of $\text{Ce}^{4+} 3d^9 4f^1 \text{ O } 2p^5$ and the doublets u/v at 901.6 and 883.0 eV corresponds to the state of $\text{Ce}^{4+} 3d^9 4f^2 \text{ O } 2p^4$. The doublets u^o/v^o , which corresponds to $\text{Ce}^{3+} 3d^9 4f^1 \text{ O } 2p^6$ final state, is absent in all samples, indicating that +4 is the dominant oxidation state. 7Mn3Ce-C support exhibits higher intensities of the doublets v'''/u''' and v''/u'' as compared to 7Mn3Ce-A sample even after adding Pd, suggesting the presence of more Ce^{4+} species in crystalline MnCeO_x samples. The relative abundance of Ce^{4+} and Ce^{3+} are estimated based on the fitted peak areas of the XPS Ce 3d spectra and listed in Table A.2.3. Despite of the predominance of Ce^{4+} , Ce^{3+} can be detected in these samples. A larger abundance of Ce^{3+} exists in 7Mn3Ce-A than in 7Mn3Ce-C. Anchoring Pd onto the support may result in more Ce^{3+} species at the expense of Ce^{4+} , which is clearly suggested by the stronger u' and v' peaks. The existence of Ce^{3+} implies the formation of oxygen vacancies since the creation of each Ce^{3+} generates two oxygen vacancies while Ce^{3+} is assumed to retain the normal coordination number of 8 as in the case of Ce^{4+} . It was suggested that the perturbation of Ce-O and/or M-O bond in $\text{CeO}_2\text{-MO}_x$ mixed oxide would form highly disordered oxygen in the lattice, promoting the oxygen transfer from the bulk to the support surface. This enhanced oxygen mobility results in more Ce^{3+} species and oxygen vacancies [28]. In a similar Ca-doped CeO_2 oxide, the Ce^{3+}

surface-enrichment was obtained by both $\text{Ca} \leftrightarrow \text{O} \leftrightarrow \text{Ce}$ interactions and O vacancies [29]. Recently, the enrichment of Ce^{3+} by Pd doping has also been reported for a Pd/MnCeO_x sample, contributing to the interaction between Pd and CeO_2 [21]. Thus, the larger abundance of Ce^{3+} in amorphous samples indicates more oxygen vacancies and enhanced oxygen mobility.

Figure A.2.6 XPS results of representative MnCeO_x samples: (a) Ce 3d; (b) Mn 2p; (c) O 1s; (d) Pd 3d.

Table A.2.3 Surface compositions calculated from XPS results of representative samples^a.

Entry	Sample	Surface atoms percentage/%				Surface Mn/Ce ratio	Relative abundance of Ce ³⁺ and Ce ⁴⁺ /%		Relative abundance of Mn ⁴⁺ and Mn ³⁺ /%			Relative abundance of O _I and O _{II} /%		Relative abundance of Pd ⁰ and Pd ²⁺ /%	
		Mn	Ce	O	Pd		Ce ³⁺	Ce ⁴⁺	Mn ⁴⁺	Mn ³⁺	AON of Mn	O _I	O _{II}	Pd ⁰	Pd ²⁺
1	7Mn3Ce-A	21.80	10.25	67.95	0	2.13	34.57	65.43	100	0	2.05	44.56	55.44	-	-
2	7Mn3Ce-C	17.61	8.97	73.42	0	1.96	19.17	80.83	67.14	32.86	1.84	76.96	23.04	-	-
3	Pd/7Mn3Ce-A	17.81	8.15	73.73	0.31	2.19	43.46	56.54	93.04	6.96	2.00	61.69	38.31	26.49	73.51
4	Pd/7Mn3Ce-C	13.97	8.06	77.49	0.48	1.73	21.59	78.41	64.99	35.01	1.82	74.41	25.59	63.91	36.09

^a The atomic ratios of the different elements were estimated using the ratio of the normalized peak intensities corrected with the atomic sensitivity factors (7.399 for Ce 3*d*, 2.420 for Mn 2*p*, 0.711 for O 1*s* and 4.462 for Pd 3*d*).

Figure A.2.6b shows the experimental and fitted Mn $2p_{3/2}$ spectra of these four samples. Previous XRD, TEM and TPR results indicated the co-existence of different manganese oxides. The peaks at round 642.2 and 640.9 eV are attributed to the presence of Mn^{4+} and Mn^{3+} species, respectively. Surprisingly, Mn^{2+} is undetectable in the fitted spectra, probably because Mn^{2+} may be partially incorporated into the fluorite structure of CeO_2 by isomorphous substitution [30]. Since only the outmost layers can be detected by XPS, this results in a higher oxidation state of Mn on the surface than in the bulk. The unobvious peak at around 645.0 eV is originated from the charge transfer between the outer electron shell of the ligand and the unfilled $3d$ shell of Mn during the creation of the core-hole in the photoelectron process [23]. Mn^{4+} is the dominant species in 7Mn3Ce-A whereas the amount of Mn^{3+} becomes considerable in 7Mn3Ce-C. Moreover, the main Mn $2p_{3/2}$ component of 7Mn3Ce-C possesses lower BE than 7Mn3Ce-A, indicating that more electrons are transferred from Ce to Mn during the co-precipitation method. Deposition of Pd slightly decreases the oxidation state of surface manganese species and the feature assigned to Mn^{3+} is discernable in Pd/7Mn3Ce-A, which may be due to the partial reduction of Mn species during MAPR synthesis. Pd/7Mn3Ce-A exhibits higher Mn BE than Pd/7Mn3Ce-C, implying that a large amount of Mn^{4+} species exists on the support surface. These changes are quantitatively reflected in Table A.2.3. The relative surface concentration of Mn^{4+} in 7Mn3Ce-A is 100% while only 67.14% is detected in 7Mn3Ce-C sample. After Pd deposition, Mn^{4+} concentration slightly declines to 93.04% and 64.99% in Pd/7Mn3Ce-A and Pd/7Mn3Ce-C, respectively. Correspondingly, the AON (average oxidation numbers) value x in MnO_x reduces from 2.05 for 7Mn3Ce-A to 2.00 for Pd/7Mn3Ce-A while it decreases from 1.84

for 7Mn3Ce-C to 1.82 for Pd/7Mn3Ce-C.

The quantitatively deconvolution of the O 1s core level spectra for all samples seems to be difficult due to the large number of oxygen species related to various cerium and manganese oxides as well as the presence of surface oxygen species such as carbonate and hydroxyl groups. Particularly, the O 1s BE for CeO₂ may shift from 529.6 to 530.3 eV, therefore overlapping with those of various MnO_x oxides ranging from 529.3 to 530.0 eV [1]. Hence, no attempt was made to analyze these components individually and the O 1s spectra were only fitted using two main features (Figure A.2.6c): i- the low BE component O_I assigned to the lattice oxygen (O²⁻) and ii- the high BE component O_{II} ascribed to other surface oxygen species (*e.g.*, chemisorbed oxygen O₂⁻ and O⁻) [13]. The amorphous samples possess higher BE of O_I component (529.8 eV) than the crystalline ones (529.5 eV), indicating that a “Mn←O” electron transfer occurs in MnCeO_x with high dispersion [15]. The relative abundance of these two oxygen components is reported in Table 3. 7Mn3Ce-A has 55.44% O_{II} component, which is nearly twice the amount in 7Mn3Ce-C. After Pd deposition, Pd/7Mn3Ce-A still has more O_{II} component than Pd/7Mn3Ce-C, though the difference is slightly smaller. The formation of O_{II} component is closely related to the nature of MnCeO_x support. Mn-O-Ce bonds, which are formed at Mn-Ce boundary by partial incorporation of Mn ions into the cubic CeO₂ structure, enhance the formation of oxide defects. Thereby, a large amount of oxygen vacancies on the surfaces of CeO₂ and MnO_x species is formed due to a high degree of coordinative unsaturation as suggested by TPR data. These vacancies act as active sites for molecular oxygen adsorption and activation, forming O_{II} species [31].

The Pd 3d XPS spectra in Figure A.2.6d consists of two asymmetric peaks assigned to Pd 3d_{5/2} and Pd 3d_{3/2} core levels which can be fitted using two doublets. The peaks at around 335.4 and 340.7 eV are attributed to metallic Pd⁰ while those at around 337.3 and 342.4 eV correspond to Pd²⁺ species. Despite of the existence of both Pd⁰ and Pd²⁺ species in both samples, Pd/7Mn3Ce-A possesses larger abundance of Pd²⁺ than Pd/7Mn3Ce-C (73.51% and 36.09%, respectively). The results discussed above have shown that 7Mn3Ce-A exhibits more surface O_{II} component as compared to 7Mn3Ce-C, which indicates a stronger oxidizing ability [1]. Thus, it can be speculated that, during the catalyst synthesis process, this active O_{II} species may be transferred from the support surface to the Pd nanoparticles, resulting in a strong interaction between Pd and MnCeO_x mixed oxides and the generation of Pd²⁺ species. Similar result was reported by Tang *et al.*, indicating that Ag⁺ species can be more stable after silver deposition onto MnO_x-CeO₂ support [12]. In addition, Pd²⁺ in both catalysts exhibits higher Pd 3d_{5/2} BEs than PdO (336.8 eV), implying a high dispersion and deficient coordination of Pd in intimate contact with MnCeO_x support as well as the subsequent promoted oxygen transfer from the support to Pd active sites [28].

A.2.2.3 Recyclability study

Recyclability is a curial factor in evaluating a heterogeneous catalyst. When the metal component is not properly anchored onto the support, it may be leached out during the course of reaction, resulting in an active homogeneous catalyst and a loss of catalytic activity on subsequent runs. The recyclabilities of both Pd/7Mn3Ce-C and Pd/7Mn3Ce-A were examined for 5 consecutive cycles, and the results are depicted in Figure A.2.7. The catalyst was recovered after each reaction run, thoroughly washed with acetone, dried at 333 K, and reused in the next

reaction. Both catalysts well maintain the high benzaldehyde selectivity and undergo a moderate decrease of the catalytic activities, which could be attributed to the loss of catalyst during the recovery.

Figure A.2.7 Recyclability of Pd/7Mn3Ce-C and Pd/7Mn3Ce-A for benzyl alcohol oxidation. Reaction conditions: catalyst, 20 mg; benzyl alcohol, 50mmol; O₂, 20 mL min⁻¹; temperature, 433 K; reaction time, 1 h.

To eliminate the effect of catalyst loss during the recovery, the recycle reactions were performed with constant metal/substrate ratio (catalyst/benzyl alcohol = 20mg/50mmol) and the results are listed in Table A.2.4. Since reaction time is 1 h, the value of quasi-turnover frequency (*q*TOF) equals to turnover number (TON) and used as catalytic activity for comparison. Obviously, the high activities of both catalysts are well maintained in 5 consecutive runs with subtle decrease. This clearly suggests that the interaction between Mn and Ce, forming either crystalline or amorphous MnCeO_x mixed oxides, not only improves the

catalytic performance but also enhances the catalyst stability and recyclability.

Table A.2.4 Recyclability of Pd/7Mn3Ce-C and Pd/7Mn3Ce-A catalysts^a.

catalyst	batch	Catalys t(mg)	Substrate (mmol)	Conv. (%)	Select.(%)			q_{TOF}^b (h ⁻¹)
					Benzal dehyde	Tolu ene	Benzo ic acid	
Pd/7Mn 3Ce-C	1	20	50	18.4	98.6	0.4	0	15325
	2	20	50	18.5	99.5	0.5	0	15381
	3	19.6	49	18.9	98.1	1.9	0	15399
	4	17.5	45	20.3	97.8	2.2	0	15190
	5	15.5	38.75	23.4	96.5	3.5	0	15078
Pd/7Mn 3Ce-A	1	20	50	20.6	99.3	0.7	0	14438
	2	20	50	20.1	98.1	1.9	0	14080
	3	19.8	49.5	20.5	98.5	1.5	0	14209
	4	17.5	45	22.5	98	2	0	14178
	5	15.2	38	26.8	97.6	2.4	0	14260

^a reaction conditions: catalyst/benzyl alcohol = 20 mg/50 mmol; O₂, 20 mL min⁻¹; temperature, 433 K; reaction time, 1 h; Carbon balance, 98.5%.

^b q_{TOF} is calculated by using the Pd content obtained from ICP.

Furthermore, characterization techniques (ICP, TEM and XPS) were introduced to carefully examine the recycled catalysts. The contents of Pd, Mn and Ce of both fresh and recycled Pd/7Mn3Ce-C and Pd/7Mn3Ce-A catalysts are listed in Table A.2.5. Evidently, the contents of Pd, Mn and Ce after 5 consecutive reaction cycles are almost the same as that of the fresh catalyst, confirming that there was no leaching of Pd and these Pd catalysts can be fully recycled.

Table A.2.5 Element analysis results of fresh and recycled representative catalysts.

Sample	Pd(wt.%)	Mn(wt.%)	Ce(wt.%)
Pd/7Mn3Ce-C	0.32	26.79	34.12
Pd/7Mn3Ce-C-R	0.31	25.43	36.48
Pd/7Mn3Ce-A	0.38	20.57	30.23
Pd/7Mn3Ce-A-R	0.40	18.61	30.25

TEM observations were carried out for the fresh and spent Pd catalysts, as depicted in Figure A.2.8. The structure and morphology of multitude of manganese oxides (MnO₂, Mn₂O₃ and Mn₃O₄) in Pd/7Mn3Ce-C is well reserved, indicating no phase change of MnO_x during the reaction. For Pd/7Mn3Ce-A, the amorphous

matrix is also well maintained with highly dispersed Pd nanoparticles. No aggregation or agglomeration of Pd nanoparticles was observed in both catalysts.

Figure A.2.8 TEM images of recycled Pd/7Mn3Ce-C (*left*) and Pd/7Mn3Ce-A (*right*).

XPS measurement was employed to examine the surface composition of these Pd catalysts. In Figure A.2.9, Pd^{2+} species disappears after reaction under solvent-free conditions, which may be due to the reduction by the alcohol substrate and further verify that Pd^0 acts as the catalytic active site [32-33]. The abundance of surface oxygen species is also examined by O 1s XPS, as depicted below. Compared to fresh samples (Table A.2.3), the concentrations of surface O_{II} species (chemisorbed oxygen O_2^- and O^-) slightly decrease. Considering the stronger oxidizing ability and higher mobility of O_{II} species, the activity loss during the recycle may also be assigned to the consumption of surface O_{II} abundance and inefficient supply.

Figure A.2.9 XPS results of recycled Pd/7Mn3Ce-C and Pd/7Mn3Ce-A catalysts (left: Pd 3d; right: O 1s).

A.2.2.4 Discussion

Our results suggested that, regardless of the structure of MnCeO_x supports (crystalline or amorphous), the catalytic performance (conversion and selectivity) and stability of Pd catalysts can be improved by combining Mn and Ce to form MnCeO_x mixed oxides. This effect is attributed to the strong synergetic interactions among MnO_x, CeO₂ and Pd. However, significant difference in the catalytic behavior appears when using different MnCeO_x support materials. Pd/7Mn3Ce-C shows higher activity than Pd/7Mn3Ce-A in the initial stage of the reaction whereas undergoes a more rapid loss of both conversion and selectivity over a long-term reaction run (Figure A.2.1). Based on the above characterization results, this different catalytic behavior can be explained considering three essential factors: texture and structure, redox properties, and surface composition.

According to the reaction kinetics, the initial reaction rate is defined as

$r_0 = -\frac{dC_A}{dt}\big|_{t=0} = -\frac{dC_{A0}(1-x)}{dt}\big|_{t=0} = C_{A0}\frac{dx}{dt}\big|_{t=0}$, where C_{A0} and x are the initial concentration and the conversion of benzyl alcohol, respectively. Thus, the initial rate is directly proportional to the slope of the tangent of the conversion curves at $t=0$. Figure 1 shows that Pd/7Mn3Ce-C has a larger slope than Pd/7Mn3Ce-A, *i.e.*, a higher initial reaction rate. The initial reaction rates r_0 are 11.5 and 8.4 mmol/h for Pd/7Mn3Ce-C and Pd/7Mn3Ce-A, respectively. Recently, Abad *et al.* have proposed a reaction mechanism in which the initial reaction rate of benzyl alcohol oxidation can be represented as $r_0=kC_{A0}C_{M0}$, where C_{M0} is the initial concentration of metal active sites. Since C_{A0} is constant at the beginning of the reaction for both catalysts, the initial rate should linearly correlate with the concentration of available metal active sites [34]. A large fraction of Pd exposed to the liquid environment results in a high availability of adsorption sites for the reactants, which may account for the high activity in the initial stage of reaction. Herein, the presence of more Pd active sites accessible to the reactants in Pd/7Mn3Ce-C than in Pd/7Mn3Ce-A, which is confirmed by XPS results, contributes primarily to the higher initial rate. A reasonable explanation can be derived from textural and structural differences of both supports. 7Mn3Ce-C support possesses a smaller surface area than 7Mn3Ce-A. Nonetheless, it is assumed that the support surface area may not be the most important factor to determine the catalytic activity since the Pd loading used in this study is quite low. The enlarged surface area of 7Mn3Ce-A is primarily due to the existence of small crystals of Mn-Ce solid solutions rather than large crystallites of Mn oxides [14]. Therefore, the relatively smaller specific surface area but larger pore diameter of crystalline support compared to amorphous support may facilitate the anchoring and deposition of Pd active species onto the support surfaces during the catalyst synthesis as well as the

transport of reactants during the reaction. Contrarily, the inferior framework (not clear) of amorphous MnCeO_x may lead to the Pd nanoparticles embedded in the matrix, suppressing the contact between Pd active sites and reactants.

Previous results demonstrate that Pd acts as the sole active element and both Pd^0 and Pd^{2+} species exist on crystalline and amorphous MnCeO_x supported Pd catalysts. To eliminate the effect of Pd content and investigate the relationship between catalytic activity and the nature of active species, the specific initial rate is introduced here: $r_{s0} = \frac{r_0}{\text{Pd content}}$. Herein, Pd/7Mn3Ce-C possesses a higher r_{s0} than Pd/7Mn3Ce-A (151316 and 110526 mmol/g_{Pd}·h, respectively). From XPS result, Pd/7Mn3Ce-C contains more surface Pd^0 species than Pd/7Mn3Ce-A, indicating that the initial reaction rate is higher when the relative amount of Pd^0 / Pd^{2+} is higher. This is in good agreement with the proposal that metallic Pd^0 is more active in the aerobic oxidation of benzyl alcohol than palladium oxide [35-36]. In the benzyl alcohol oxidation over Pd/Al₂O₃ catalysts, Pd is in reduced state (Pd^0) even in the presence of oxygen, which is attributed to the strong reducing character of benzyl alcohol [37]. Our previous study also showed that Pd catalyst supported on CNT only consists of metallic Pd^0 species after reaction [32]. Thus, metallic Pd^0 species is responsible for the high catalytic activity. When Pd^{2+} is the primary component, an long induction period was essential to transform the supported Pd^{2+} species to metallic Pd nanoparticles, *i.e.*, the true active species [33]. Herein, Pd/7Mn3Ce-A consists of larger amounts of Pd^{2+} than Pd^0 , exhibiting a low initial catalytic activity. Therefore, it can be concluded that the initial reaction activity is intimately related to the accessibility of exposed Pd active sites and surface Pd^0 concentration.

Despite of a low initial reaction activity, Pd/7Mn3Ce-A shows an enhanced

catalyst stability and resistance against deactivation, which can be interpreted from the redox properties and surface composition of the support. The support does not directly influence the dehydrogenation step but affects the adsorption, activation and transfer of oxygen, which also has a strong effect on the activity. Previous characterization results have shown that 7Mn3Ce-A support possesses larger abundance of oxygen vacancies and surface O_{II} species (chemisorbed oxygen O_2^- and O^-). O_{II} species have stronger oxidizing ability and higher mobility, which contribute to the enhanced oxygen transfer and redox cycle via facile transformation of the lattice oxygen O^{2-} due to abundant oxygen vacancies accompanied by the formation of Ce^{3+} species (not clear) [1]. During the oxygen transfer, these short-lived but highly active chemisorbed oxygen species, O_2^- and O^- , can be rapidly activated by diffusing into the CeO_2 lattice vicinity and converted into lattice oxygen O^{2-} [38]. Due to the high oxygen mobility in 7Mn3Ce-A support, the vacancies around Pd nanoparticles after consuming the lattice oxygen O^{2-} are rapidly replenished by oxygen spillover from the bulk of the support, and the oxygen distribution on the surface is equilibrated. On the other hand, the replenishment of oxygen in 7Mn3Ce-C support, which has lower oxygen mobility and less oxygen vacancies, mainly comes from the gas phase. Under such an insufficient oxygen supply, Pd active sites would be covered with hydrogen and carbonaceous deposits and deactivated, leaving only the sites for decarbonylation still active [39]. Thus the generation of benzaldehyde would be suppressed and the decomposition and further oxidation of carbonyl product would take place, leading to a lower activity and selectivity over Pd/7Mn3Ce-C catalyst. Besides, the presence of more oxygen vacancies and surface O_{II} species in amorphous support as well as more Mn ions in high oxidation state (Mn^{4+}) also contributes

significantly to the oxygen transfer. In contrast to the Ce surface-enrichment and the remarkably low surface dispersion of Mn in crystalline MnCeO_x samples, amorphous MnCeO_x support materials exhibit a homogeneous dispersion of Mn^{4+} and Ce^{4+} ions [23]. Mn species in higher oxidation states can facilitate the redox cycles and improve the oxygen mobility and availability, resulting in an enhanced catalytic activity [1, 8, 40]. Moreover, the enhanced redox properties exhibited by MnCeO_x can promote the reversible sorption/desorption cycles of lattice oxygen [25]. Therefore, the mutual promotion between redox properties and oxygen mobility lead to an enhanced catalyst stability and lower deactivation in the selective oxidation of benzyl alcohol [16].

Catalytic results show that Pd/MnCeO_x catalyst can effectively suppress the formation of toluene, giving high benzaldehyde selectivity. In order to clarify the origin of toluene formation and the mechanism of benzyl alcohol oxidation, catalytic tests were conducted in N_2 atmosphere over Pd/7Mn3Ce-C and Pd/7Mn3Ce-A catalysts, respectively. Under such anaerobic condition, both catalysts exhibit catalytic activities of 0.9% conversion (Table A.2.1, entries 12-13), implying the existence of a dehydrogenation mechanism in which benzaldehyde formation occurs in the absence of oxygen. Benzyl alcohol is mainly converted to benzaldehyde (toluene selectivities are 2.1% and 1% for Pd/7Mn3Ce-C and Pd/7Mn3Ce-A , respectively). The formation of toluene is rather complex and has been extensively investigated. Besides the hydrogenolysis of benzyl alcohol [37], toluene can also be originated from the disproportionation of benzyl alcohol, yielding equimolar mixture of benzaldehyde and toluene [41-43]. Moreover, Jayamani *et al.* also demonstrated that toluene can be formed by the decomposition of dibenzyl ether [44]. Since no ether is detected in the present study, this route can

be ruled out. Therefore, the negligible production of toluene under anaerobic condition clearly suggests that toluene is formed by hydrogenolysis of benzyl alcohol rather than by disproportionation and benzyl alcohol oxidation follows most likely a dehydrogenation mechanism.

Based on the conventional dehydrogenation mechanism, an integrated alcohol oxidation mechanism over Pd/MnCeO_x is proposed (Scheme A.2.1). In this mechanism, Pd acts as the sole catalytic center where the reaction takes place and the oxygen transfer is completed through the support via a redox cycle. Benzyl alcohol is adsorbed on Pd nanoparticles, forming a metal-alkoxide intermediate and adsorbed hydrogen via O-H bond cleavage. Then, it is further converted to benzaldehyde through β -hydrogen elimination as the rate-limiting step, leaving reduced Pd sites partially covered by hydrogen, *i.e.*, Pd-hydride. The adsorbed oxygen on support surface dissociates into chemisorbed oxygen species O₂⁻ and O⁻, diffuses into the support lattice vicinity, and subsequently is activated at the oxygen vacancies and converted into lattice oxygen O²⁻, accompanied by the transformation of Ce³⁺ to Ce⁴⁺. The lattice oxygen is further transferred through the oxide defects in MnCeO_x supports and migrates to the interface between the support and Pd active sites. Finally, it reacts with Pd-hydride to regenerate Pd active sites, forming H₂O as product. The poor catalytic activity over mixture of Pd/CeO₂ and Pd/MnO_x catalysts (entry 11, Table A.2.1) verifies that this oxygen migration can be facilitated only over MnCeO_x mixed oxides rather than over the physical mixture. The dehydrogenation-oxidation of benzyl alcohol is completed via a synergetic redox cycle and electron transfer involving Pd, Mn and Ce: Pd $\leftrightarrow$ Mn $\leftrightarrow$ Ce. A similar consecutive oxygen transfer mechanism was also proposed in a Ag/MnO_x-CeO₂ system, in which oxygen is transferred from the

oxygen reservoir of CeO_2 to activate Ag_2O sites through MnO_x [12]. Consequently, the synergetic interactions among Pd, MnO_x and CeO_2 are enhanced due to the mutual promotion of texture and structure, redox properties, and surface composition, leading to an improved catalytic activity and higher resistance against deactivation.

Scheme A.2.1 Overall reaction mechanism for benzyl alcohol oxidation over Pd/ MnCeO_x catalysts.

A.2.3 Conclusions

In this work, both crystalline and amorphous MnCeO_x supports were successfully synthesized by co-precipitation and redox-precipitation methods, respectively. Pd was subsequently deposited by a facile MAPR procedure, leading to the formation of highly dispersed Pd nanoclusters. MnCeO_x supports remarkably enhanced both the catalytic activity and selectivity in the aerobic oxidation of benzyl alcohol compared to the single MnO_x and CeO_2 oxides. The highest $q\text{TOFs}$ were achieved over Pd/7Mn3Ce-C ($15\,235\text{ h}^{-1}$) and Pd/7Mn3Ce-A ($14\,438\text{ h}^{-1}$), and the activity can be maintained over five consecutive reaction runs. Pd acts as the sole active component and the enhanced catalytic activity can be

attributed to the synergetic interactions among Pd, MnO_x and CeO₂. Good accessibility of Pd active sites and high concentration of surface Pd⁰ contribute to the high initial reaction rate over crystalline MnCeO_x supported Pd catalyst. Amorphous MnCeO_x supported Pd catalyst exhibits an enhanced catalyst stability and lower deactivation due to the mutual promotion between redox properties and oxygen mobility. This work has been published in Journal of Catalysis (Chen *et al.* Journal of Catalysis, 2011, 283 (1), 34-44); reuse in this chapter is under the permission of Elsevier Global Rights Department.

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A.3 Journal publications and conference presentations

Journal publications

1. Yuanting Chen, Houpeng Wang, Chang-jun Liu, Zzhiyuan Zeng, Hua Zhang, Chunmei Zhou, Xinli Jia, Yanhui Yang*, Formation of monometallic Au, Pd and bimetallic Au-Pd nanoparticles confined in mesopores via Ar glow discharge plasma reduction and their catalytic applications in aerobic oxidation of benzyl alcohol, Journal of Catalysis, doi:10.1016/j.jcat.2012.01.020.
2. Yuanting Chen, Huijian Zheng, Zhen Guo, Chunmei Zhou, Chuan Wang, Armando Borgna*, Yanhui Yang*, Pd catalysts supported on MnCeO_x mixed oxides and their catalytic application in solvent-free aerobic oxidation of benzyl alcohol: support composition and structure sensitivity, Journal of Catalysis, 2011, 283 (1), 34-44.
3. Yuanting Chen, Linlu Bai, Chunmei Zhou, Jong-Min Lee, Yanhui Yang*, Palladium-catalyzed aerobic oxidation of 1-phenylethanol in an ionic liquid additive, Chemical Communications, 2011, 47(22), 6452-6454.
4. 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, 2011, 141, 149-157.
5. Yuanting Chen, Zhen Guo, Tao Chen, Yanhui Yang*, Surface-functionalized TUD-1 mesoporous molecular sieve supported palladium as a catalyst for solvent-free aerobic oxidation of benzyl alcohol, Journal of Catalysis, 2010, 275, 11-24.
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monometallic and Au-Pd bimetallic catalysts supported on SBA-16 mesoporous molecular sieves, *Applied Catalysis A: General*, 2010, 380(1-2), 55-65.

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10. Chunmei Zhou, Yuanting Chen, Zhen Guo, Xin Wang*, Yanhui Yang*, Promoted aerobic oxidation of benzyl alcohol on CNT supported platinum by iron oxide, *Chemical Communications*, 2011, 47 (26), 7473-7475.

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14. Shuangquan Hu, Dapeng Liu, Chuan Wang, Yuanting Chen, Zhen Guo, Armando Borgna, Yanhui Yang*, Liquid-phase epoxidation of trans-stilbene and cis-cyclooctene over vanadium-exchanged faujasite zeolite catalysts, *Applied Catalysis A: General*, 2010, 386, 74-82.
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17. Qinghu Tang, Yuanting Chen, Yanhui Yang*, Understanding the nature of vanadium species supported on activated carbon and its catalytic properties in the aerobic oxidation of aromatic alcohols, *Journal of Molecular Catalysis A: Chemical*, 2010, 315(1-2), 43-50.
18. Qinghu Tang, Xiaona Huang, Chengming Wu, Peizheng Zhao, Yuanting Chen, Yanhui Yang*, Structure and catalytic properties of K-doped manganese oxide supported on alumina, *Journal of Molecular Catalysis A: Chemical*, 2009, 306, 48-53.
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21. Qinghu Tang, Yuanting Chen, Caixia Jasmine Zhou, Tao Chen, Yanhui Yang*, Statistical modeling and analysis of the aerobic oxidation of benzyl alcohol over K-Mn/C catalysts, *Catalysis Letters*, 2009, 128(1-2), 210-220.

Conference presentations

1. Yuanting Chen, Yanhui Yang*. Benzyl alcohol oxidation over Au-Pd nanoparticles confined in mesoporous molecular sieves. *The 15th National Conference on Catalysis of China (15th NCC)*, Guangzhou, China, Dec 2010 (Oral presentation).
2. Yuanting Chen, Yanhui Yang*. Solvent-free aerobic oxidation of benzyl alcohol over Pd monometallic and Au-Pd bimetallic catalysts supported on SBA-16 mesoporous molecular sieves. *The International Symposium on Advanced Bio, Nano, and Pharmaceutical Science and Technology (BNPST 2010)*, Singapore, May 2010 (Oral presentation).
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5. Yuanting Chen, Qinghu Tang, Yanhui Yang*. Aerobic oxidation of aromatic alcohols over gold-palladium alloy catalyst supported on SBA-16 mesostructured silica. *The International Symposium on Advanced Bio, Nano, and Pharmaceutical Science and Technology (BNPST 2009)*, Beijing, China, May 2009 (Oral presentation).
6. Qinghu Tang, Yuanting Chen, Yanhui Yang*, Role of potassium in the aerobic oxidation of aromatic alcohols over K⁺-promoted Mn/C catalysts. *15th Regional Symposium on Chemical Engineering in conjunction with 22nd Symposium of*

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