Design of palladium-based heterogeneous catalysts for selective oxidation of alcohols

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**DESIGN OF PALLADIUM-BASED
HETEROGENEOUS CATALYSTS FOR SELECTIVE
OXIDATION OF ALCOHOLS**

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Abstract

Selective oxidation of alcohols into their corresponding aldehydes and acetones have always been an important issue in chemical engineering as the obtained products are essential raw materials for the synthesis of other fine chemicals. Particularly, the selective oxidation of benzyl alcohol to benzaldehyde has attracted much interest in the last several decades due to the importance of benzaldehyde as a precursor for the synthesis of other fine chemicals. Similarly, ethanol selective oxidation produces a variety of oxide products including acetaldehyde, acetone, acetic acid, ethylene oxide, diethyl ether and ethyl acetate, many of which are of paramount importance in chemical industry.

Much efforts have been devoted to producing highly selective carbonyl compounds with high yields in the past several decades. One significant improvement in alcohol transformation reaction is the evolution of oxidants. Primarily, stoichiometric quantities of expensive inorganic reagents including ruthenium oxides, chromium reagents, permanganates and some others are employed as oxidants. Now inexpensive, environmentally benign oxidants like pure oxygen, hydrogen peroxide are used.

Another big improvement, also the most important step in catalytic engineering is to choose the appropriate catalysts. In this dissertation, a series of palladium catalysts supported on commercial available titanium dioxide nanoparticles and titanium dioxide nanowires synthesized by a molten salt flux method are prepared by two common methods, urea-assisted deposition-precipitation and incipient wetness impregnation methods. Selective oxidation of benzyl alcohol was employed as a model reaction to investigate the performance of as-prepared catalysts. It is found that catalysts prepared

by the impregnation method have larger metal loadings with a broader size distribution than that prepared by the deposition-precipitation method, resulting in much higher activity with lower selectivity towards benzaldehyde. The lower loadings of palladium nanoparticles using deposition-precipitation method was due to the greater repulsion between support materials and palladium complex at elevated pH. The influences of reaction parameters including reaction temperature, reaction duration, catalysts/substrate molar ratio and oxygen flow rate are studied. For all the catalysts, benzyl alcohol can be transformed by two seemingly independent routes, with benzaldehyde the main product. No further oxidative compounds are obtained, suggesting the excellent controllability of as-prepared catalysts in inhibiting deeper oxidation reaction. It is believed initially only the disproportionation route is active and as the reaction proceeds, the oxidation reaction is triggered, gradually match and finally exceeds the disproportionation route. Due to the existence of mass transfer problems, all of them have their own optimum reaction parameters for catalysts/substrate weight ratio and oxygen flow rates. Also, catalytic results showed that water is the main reason for catalysts deactivation and removal of the toluene produced at early stages in time might be able to fully inhibit the disproportion route, resulting in almost 100% selectivity towards aldehyde. Although catalysts based on titanium dioxide nanoparticles have better activity compared to their nanowire counterparts, much lower aldehyde selectivity is its main disadvantage. With 100% selective towards benzaldehyde and excellent stability, further modification of palladium catalysts supported on titanium dioxide nanowire have the potential to be used in large-scale synthesis of benzaldehyde through benzyl alcohol oxidation.

The introduction of basic sites can greatly improve the adsorption and dispersion of noble metal catalysts to the supporting materials, thus modify the catalytic activity. In this thesis, a series of nitrogen-doped carbon nanotubes were successfully prepared using commercial available carbon nanotubes under a mild hydrothermal reaction system. Different kinds of nitrogen sources, including hydrazine hydrate coupled with ammonia, urea, hexamethylenetetramine, dicyandiamide, hydroxylamine chloride, are employed to modify the interesting tubular structure. It was demonstrated that different nitrogen sources can change the chemical and electronic properties of pristine carbon nanotubes with different extents. Palladium ions have a greater tendency to absorb on the modified CNTs due to the existence of various types of nitrogen atoms, resulting much higher activity and higher selectivity towards aldehyde compared to its unmodified counterparts. To better understand the evolution of nitrogen doping, nitrogen-doped carbon nanotubes prepared with increased weight ratios of hydroxylamine chloride towards carbon nanotubes are prepared. All the palladium nanoparticles supported on modified carbon nanotubes have a smaller mean size and narrower distribution compared to unmodified ones. Even quite a small amounts of HAcI can decrease both of them by half. With the increase of HAcI, gradually bigger particles are obtained while the distribution can be maintained. When appropriate amounts of nitrogen sources are used, dramatic changes resulting abnormally larger particles are achieved. Such changes can also be reflected by the activity towards benzyl alcohol oxidation. Changes in benzyl alcohol conversion have exactly the same pattern as that of the mean particle size, with almost 2.5 times enhancement for 2Pd@CNT-HAcI-3. Different from the trend in conversion, monotonically increase in

benzaldehyde selectivity is observed until 100% is realized over 2Pd@CNT-HACl-5 catalysts. These results suggest gradually changes in carbon nanotubes can be realized by choosing appropriate type of nitrogen source and tuning reaction conditions through a simple and easy hydrothermal reaction, and the resulting carbon nanotubes are promising supporting materials for other oxidation reactions.

A series of Pd/HY bifunctional catalysts have been successfully prepared with deposition-precipitation method for selective oxidation of ethyl alcohol using molecular oxygen as an efficient oxidant. The properties of these catalysts were examined through TEM, XRD, FTIR, TGA and stability test. Characterization results proved that Pd nanoparticles are effective in suppressing the coke deposition in ethanol selective oxidation and a small amount of coke deposited on the catalyst may enhance the stability due to the suppressed Pd nanoparticle agglomeration. In conclusion, Pd/HY bifunctional catalyst was demonstrated as a unique catalyst for ethanol oxidation to afford high yield one-step synthesis of acetaldehyde and ethyl acetate, especially the ethyl acetate formation, 91.8% of ethyl acetate selectivity at 150 °C and 84.2 % of ethyl acetate yield were achieved over 2Pd/HY catalyst at 210 °C. The product selectivity can be readily tuned by changing the reaction condition parameters. The reverse hydrogen spillover effect was identified to take place between Pd nanoparticles and zeolite support, which can well balance the oxidative activity and acidity at an appropriate reaction temperature. Pd/HY catalyst was remarkably stable at low reaction temperature during the reaction and only a small amount of coke was deposited.

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Chapter 1 Background and Philosophy

1.1 Background and the Driving Force for Heterogeneous Catalysis in Alcohol Selective Oxidation

Selective oxidation of alcohols into their corresponding aldehydes and acetones have always been an important issue in chemical engineering as the obtained products are essential raw materials for the synthesis of other fine chemicals. As one of the oxidized derivatives of benzyl alcohol, benzyl aldehyde has attracted much interest in the last several decades due to its importance as a precursor for the synthesis of other fine chemicals, spanning from pharmaceutical, dyestuff, agrochemical, perfume industries, biomass conversion. Another reason is its simplicity as a model reaction to investigate the mechanism involved and to test the activity of catalysts. Currently, it is largely produced through the selective oxidation of toluene or liquid phase hydrolysis of benzyl chloride [1]. However, its drawbacks are also apparent: harmful reagents, complicated manufacturing steps, chlorine-contamination and low products yields. A promising alternative path is the selective oxidation of benzyl alcohol which is relative reactive compared to other primary alcohols.

In the global attempt to reduce carbon footprint, the chemical and petrochemical industry face the problem to replace the currently used fossil feedstocks with renewable resources. A viable alternative, gaining acceptance in recent years, is biomass-based alcohols, especially bio-ethanol. Bio-ethanol is a renewable energy source that can be easily produced from many biomass sources, including energy plants, grains, and waste materials of the agricultural and forestry industries and even from the organic fraction of municipal solid wastes. It is widely available, easy to store and transport and safe to

handle. Ethanol selective oxidation produces a variety of oxide products including acetaldehyde, acetal, acetone, acetic acid, ethylene oxide, diethyl ether and ethyl acetate, many of which are of paramount importance in chemical industry. Transition metal oxides, noble metal-based materials, zeolites, octahedral molecular sieves have been widely studied in ethanol selective oxidation reactions.

Much efforts have been devoted to producing highly selective carbonyl compounds with high yields in the past several decades. One significant improvement in alcohol transformation reaction is the evolution of oxidants. Primarily, stoichiometric quantities of expensive inorganic reagents including ruthenium oxides [2, 3], chromium reagents [4-7], permanganates [8, 9] and some others [10, 11] are employed as oxidants. Although they are capable of reacting with a range of alcohols, the disadvantages are also apparent: hazardous to prepare and difficult to separate from the products; low conversion with poor selectivity. Also, accompanying the reaction are usually environmentally polluting metal wastes, which is a big burden for the environment. Therefore, looking for inexpensive, environmentally benign oxidants has becoming more and more important. Hydrogen peroxide, air or pure oxygen are the perfect choice. They are cheap, and environmentally friendly. More importantly, the sole byproduct in these alcohol oxidations is water and by employing appropriate catalysts, they can transform a variety of alcohols with both high activity and high selectivity.

Another big improvement, also the most important step in catalytic engineering is to choose the appropriate catalysts. Many transition metal-based homogenous catalytic systems, both reactants and catalyst are in the same phase, have been developed and improved in the last several decades, ranging from inexpensive ones to noble metals.

Typical examples include cobalt-based Co-nitro complexes [12], $\text{Co}(\text{acac})_3$ [13, 14], Co(II)-Schiff base [15-17] and Co-phthalocyanine [18, 19] catalysts, copper-based catalysts Cuprous chloride (CuCl) [20], $\text{CuCl}/\text{phen}/\text{DBAD}$ catalytic system, iron-based as $\text{Fe}(\text{NO}_3)_3$ and FeBr_3 binary catalysts [21], vanadium-based oxovanadium complexes [22, 23] and V_2O_5 [24]. However, these non-noble metal catalysts often suffer from large loadings or forcing conditions, which are the main disadvantages compared to another group of great interest, the noble metal-based catalysts. Gold [25], ruthenium, palladium are the most popular ones among them. Ruthenium-based catalysts include tetrapropylammonium perruthenate [26], $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2/\text{hydroquinone}$ [27], $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2/\text{hydroquinone}$ [28, 29], $[\text{RuCl}_2(\text{p-cymene})]_2/\text{Cs}_2\text{CO}_3$ [30], $(\text{ON})\text{Ru}(\text{salen})$ complex [31, 32]. Although its ability to oxidize secondary alcohols was discovered in 1977 [33], it was not until 20 years later, when a series of palladium-based catalysts have shown great potential in selective transformation of organic chemicals, that it became the focus again. Such catalytic systems include Pd(II)-hydrotalcite catalysts [34-36], $\text{Pd}(\text{OAc})_2$ catalysts [37-39], and many others [40-42].

Homogeneous catalytic systems are usually more reactive and selective compared to their heterogeneous counterparts, reactions of which take place on the surface of the catalysts. However, they often suffer from shorter life, low thermal stability, difficult and tedious separation and recovery procedure, which can add to the cost especially when noble metal-based catalysts are employed [36, 43]. Therefore, a variety of heterogeneous catalysts based on transition metal [44] especially the noble ones have also been developed to catalyze the oxidation of benzyl alcohol.

Silver supported on hydrotalcite (HT, $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$) has been employed by Mitsudome to selective oxidize benzyl alcohol under oxidant- and additive-free conditions [45], which can selectively convert benzyl alcohol into benzaldehyde with benzyl benzoate as byproduct through a dehydrogenation step. Silver supported on different metal oxides have also been prepared and investigated for benzyl alcohol oxidation [46, 47]. Besides silver, ruthenium is also applicable to benzyl alcohol oxidation. Ruthenium supported on hydroxyapatite [48], alumina [49], silica, iron oxide [50] and carbon nanotubes [51] have showed good activity in benzyl alcohol transformation. Different solvents such as toluene, trifluorotoluene, water or its mixtures, and oxygen pressure can play a vital rule. Another common used noble metal is gold. Fang et al has successfully prepared gold catalysts with controlled size supported on different supporting materials and studied their activity in oxidant-free benzyl alcohol dehydrogenation [52]. Last but not least, palladium-based catalysts supported on different materials have also shown superior activity in benzyl alcohol oxidation. Compared to aforesaid systems based on various transition metals, the effect of supports are more profound.

1.2 Motivation and Outline of This Dissertation

For selective oxidation of benzyl alcohol and ethyl alcohol reactions based on noble-metal heterogeneous catalyst, the particle size, supporting materials, the solvent systems as well reaction temperature can have a profound influence in the activity as well as the selectivity. For particle size effect, the structure sensitivity effect can be attributed to the fact that coordinatively unsaturated atoms like corner atoms and face atoms are the ones that directly make contact and react with the substrate. Therefore, the relative

abundance of them determines the activity of the catalysts. For the supporting materials effect, acidic and basic sites can act as promoters to be involved into the reaction. Appropriate solvents can separate the products from the catalysts, thus preventing the deactivation of the catalysts.

Due to its intrinsic and tunable photoelectric properties [53], titanium dioxide can be found applications in “energy” and “environmental” fields. Besides, it can also be used in photovoltaic devices which convert solar energy into electricity power. Being inexpensive, nontoxic, highly stable chemically and optically, corrosion resistant, environmentally friendly [54], titanium dioxide can also be used in the “environmental” field. Despite the aforementioned applications in the later developed functional as well as conventional areas, titanium dioxide can also be utilized to the classical catalysis field, mostly as support material for noble metal catalysts. Hutchings discovered apart from the particle size, catalyst and support interaction, the ratio of gold and palladium can have a profound impact on the conversion as well as the selectivity of alcohol oxidations [55]. Thus, in this dissertation, palladium catalysts, which is widely used in alcohol oxidation reaction, will be prepared in two ways using commercial titanium dioxide and titanium dioxide nanowires as supporting materials to investigate the effects of temperature, reaction duration, catalysts weight/substrate ratio, oxygen flow rate and supporting materials.

Based on the number of graphenic layers in a nanotube, carbon nanotubes can be categorized into single-walled carbon nanotube (SWCNT), double-walled carbon nanotube (DWCNT), and multi-walled carbon nanotube (MWCNT). It has been both theoretically predicted and experimentally measured, carbon nanotubes have high

Young's modulus and tensile strength. Thus, carbon nanotubes can be used to enhance the mechanical strength of composite materials. Besides, similar to graphite and diamond, carbon nanotubes also have low heat capacity and high thermal conductivity [56]. More importantly, carbon nanotubes are widely used as a supporting material due to its high thermal stability, large surface area and tubular characters. It has been proven that the surface functionalization of carbon nanotubes with amino groups can greatly affect its interaction with the noble metal catalysts, thus resulting in different catalytic performances according to the abundance of basic groups [57]. Another kind modification is more violent. Post treatment of carbon nanotubes with different nitrogen sources can successfully incorporate nitrogen atoms into the lattice, resulting in great change in its physical and chemical properties. In this dissertation, nitrogen-doped carbon nanotubes will be used as supporting materials to investigate the performance of palladium catalysts in the selective oxidation of benzyl alcohol.

Zeolites, typically defined as hydrated, crystalline tectoaluminosilicates that are constructed from TO_4 tetrahedra, have been comprehensively used in oil processing, ion-exchange, guest-storage, hydrocarbon conversion, molecular recognition/sensing, size/shape selective heterogeneous catalysis, gas processes due to their unique physical and chemical properties since Barrer and coworkers successfully prepared the first synthetic zeolites in 1940s. Underpinning all these applications are the well-defined pore structure, high thermostability and remarkable acidic properties of zeolites.

In our group, supported Pd has been proved as efficient catalysts for selective oxidation of benzyl alcohol, showing remarkably high selectivity towards to benzaldehyde. Different supports significantly affected Pd activity and selectivity. The

lowed surface acidity surrounding the Pd nanoparticles improved the catalytic activity in benzyl alcohol dehydrogenation. A redox support such as MnCeO_x mixed oxide effectively enhanced the stabilization of Pd nanoparticles along with the improved oxygen activation. Herein, we investigated the gas-phase aerobic oxidation of ethanol to ethyl acetate through acetaldehyde intermediate (self-coupling mechanism) over zeolite supported Pd metallic nanoparticles. The influence of interaction between zeolite acidic site and oxidative center of Pd on the selectivity and consequently product distribution is also studied. To further investigate and verify the effect of reverse hydrogen spillover on the unique catalytic activity and selectivity of Pd/HY catalyst in the aerobic oxidation of ethanol for ethyl acetate production, control experiments such as reactions under different temperatures, the reactions over different metals and different zeolite materials were carried out.

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Chapter 2 Literature Review

2.1 Selective Oxidation of Alcohols

Selective oxidation of alcohols into their corresponding aldehydes and acetones have always been an important issue in chemical engineering as the obtained products are essential raw materials for the synthesis of other fine chemicals. Much efforts have been devoted to producing highly selective carbonyl compounds with high yields in the past several decades. The main improvements can be classified into two fields: the evolution of oxidants and the selection of appropriate catalysts.

2.1.1 The Evolution of Oxidants

One significant improvement in selective alcohol transformation reaction is the evolution of oxidants. Primarily, stoichiometric quantities of expensive inorganic reagents are often employed as oxidants. Typical examples includes ruthenium oxides, chromium reagents, and permanganates. Ruthenium-based oxidants including Ru(VIII) oxides like ruthenium tetroxide [1], Ru(VII) oxides like $(Bu_4N)[RuO_4]$ ('TBAP') and $(Pr_4N)[RuO_4]$ ('TPAP'), Ru(VI) oxides like $(PH_4P)[RuO_2Cl_3]$ and $[RuO_2(COMe)(py)_2]$, ruthenium (V) complexes, oxoruthenium (IV) complexes, and ruthenium (III) compounds have shown different activity and selectivity in alcohol oxidation reactions [2]. Solid potassium permanganate and sodium permanganates can also transform a variety of alcohols into their corresponding carbonyl compounds [3, 4]. Another type of extensively used oxidants is chromium reagents, including chromium (VI) oxide-pyridine complex [5], sodium dichromate [6], and other chromium compounds [7, 8]. Some other compounds have also been studied [9, 10]. Although they are capable of reacting with a range of alcohols, the disadvantages are also apparent:

hazardous to prepare and difficult to separate from the products [6]; low conversion with poor selectivity. Also, accompanying the reaction are usually environmentally polluting metal wastes, which is a big burden for the environment. Therefore, looking for inexpensive, environmentally benign oxidants has becoming more and more important. Hydrogen peroxide, air or pure oxygen are the perfect choice. They are cheap, and environmentally friendly. More importantly, the sole byproduct in these alcohol oxidations is water and by employing appropriate catalysts, they can transform a variety of alcohols with both high activity and high selectivity.

2.1.2 Homogeneous Catalytic Systems for Alcohol Oxidations

The first step, also the most important step in catalytic engineering is to choose the appropriate catalysts. Homogeneous catalytic systems, in which both reactants and catalyst are in the same phase, are usually more reactive and selective compared to their heterogeneous counterparts, reactions of which take place on the surface of the catalysts. However, they often suffer from shorter life, low thermal stability, difficult and tedious separation and recovery procedure, which can adds to the cost especially when noble metal-based catalysts are employed [11, 12]. Therefore, in the next few chapters, the evolution from homogeneous catalysts to heterogeneous catalysts will be discussed, including both non-noble metal- and noble metal-based catalytic systems. At the same time, the intrinsic mechanisms will also be investigated.

2.1.2.1 Non-noble Transition Metal-based Catalytic Systems

Many transition metal-based homogenous catalytic systems have been developed and improved in the last several decades, ranging from inexpensive ones to noble metals. For example, Co-nitro complexes can be activated by Lewis acids to transform primary

and secondary alcohols into aldehydes and ketones respectively [13]; N-hydroxyphthalimide (NHPI) combined with $\text{Co}(\text{acac})_3$ can effectively oxidize secondary alcohols and *vic*-diols with oxygen under mild conditions [14, 15]. In addition, Co(II)-Schiff base [16-18] and Co-phthalocyanine [19, 20] catalysts were found effective in converting secondary alcohols into corresponding carbonyl compounds. These catalytic systems are usually conducted under mild conditions with low catalysts loadings, which is a big advantage [21]. Apart from cobalt, copper-based catalysts also show activity in oxidizing various alcohols. Cuprous chloride (CuCl) can selectively transform primary alcohols into aldehydes with oxygen under the mediation of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) [22]. With the addition of N-methylimidazole (NMI), the $\text{CuCl}/\text{phen}/\text{DBAD}$ catalytic system (phen=1,10-phenanthroline, DBAD=di-tert-butylhydrazine-1,2-dicarboxylate) developed by Markó can effectively catalyze the oxidation of all classes of alcohols [23-27]. More recently, copper catalysts are found to be able to chemoselectively oxidize primary alcohols regardless of the presence of other secondary counterparts when ligands such as 2,2'-bipyridine [28, 29] or salen-type ligands [30] are used. Of note, contrary to cobalt-based catalysts, cu-based catalytic systems prefer to transform primary alcohols rather than secondary ones. However, iron salts such as $\text{Fe}(\text{NO}_3)_3$ and FeBr_3 binary catalysts have been reported to selectively oxidize secondary and benzylic alcohols using oxygen as sole oxidant [31], which is quite the opposite of copper-based catalysts. Further medication of the system with TEMPO and NaNO_2 can enlarge the substrates to include secondary benzylic and aliphatic alcohols as well as alcohols containing N,S heteroatoms [32]. Another well-studied transition metal catalysts is vanadium. Nemoto reported the successful synthesis

of oxidation of α -dicarbonyl compounds through the oxidation of α -hydrocarbonyls using various trichlorooxyvanadium catalysts in 1999 [33]. Uemura studied a series of oxovanadium complexes and the effect of solvent on the oxidation of propargylic alcohols [34, 35], founding $\text{VO}(\text{acac})_2$ show better activity than other counterparts and the acetonitrile the best solvent. Interestingly, using K_2CO_3 in toluene, V_2O_5 can react with various primary and secondary alcohols, including aliphatic and benzylic alcohols, into its corresponding carbonyl compounds [36].

2.1.2.2 Noble Transition Metal-Based Catalytic Systems

Another group of interest is the noble metal-based catalytic systems, in which gold, ruthenium, palladium are the most popular. For gold-based catalysts, Guan et al investigated the effect of different oxidants on the selective oxidation of benzyl alcohol using toluene as solvent and found that oxygen has the best performance among the three. Subsequent applications in other alcohols oxidation confirms the effectiveness of AuCl with an anionic ligand [37]. Compared to gold, ruthenium has attracted more interest due to its versatility to react with different kinds of alcohols. Markó [38] and Ley [39, 40] successfully employed tetrapropylammonium perruthenate (TPAP) as catalysts to transform various first and second alcohol to corresponding aldehydes and ketones, which is much more simple, efficient and versatile than other procedures. Other ruthenium-based catalytic systems have also been developed, such as the application of $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2/\text{hydroquinone}$ in primary alcohols oxidation [41], $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2/\text{hydroquinone}$ in primary and secondary alcohols oxidation [42, 43], $[\text{RuCl}_2(\text{p-cymene})]_2/\text{Cs}_2\text{CO}_3$ in benzylic and allylic alcohols oxidation [44], $(\text{ON})\text{Ru}(\text{salen})$ complex in chemoselective oxidation of primary alcohols [45, 46],

chiral (ON)-Ru(salen) complexes in transformation of meso-diols [47], showing the extraordinary abilities of ruthenium in selective alcohol oxidation. Last but not least, palladium is not only the most extensively studied catalysts, but also the most mature one in selective oxidation of alcohols [21]. Although its ability to oxidize secondary alcohols was discovered in 1977 [48], it was not until 20 years later, when a series of palladium-based catalysts have shown great potential in selective transformation of organic chemicals, that it became the focus again. Such catalytic systems include Pd(II)-hydrotalcite catalysts used to oxidize a wide range of saturated alcohols as well as unsaturated ones [12, 49, 50], Pd(OAc)₂ catalysts to transform a variety of primary and secondary alcohols [51-53], and many others [54-56]. The generally-accepted mechanism can be depicted in Figure. 2, which involves four steps: alcohol binding, deprotonation, β -hydride elimination and reoxidation [21].

Figure 2.1 Generally accepted mechanism for palladium-catalyzed alcohol oxidation [21].

In summary, non-noble and noble transition metal-based homogeneous catalytic systems have been extensively studied for the selective oxidation of various alcohols. Some of them show versatility in transforming a large range of alcohols while some are only active to react with specific type of alcohols. The reaction conditions, including solvents, bases promoters, reaction temperature, can play a vital role in controlling the selectivity to specific products. However, for non-noble metal catalysts, large loadings are often necessary. Also, the post separation of catalysts and products are very tedious and time-consuming.

2.1.3 Heterogeneous Catalytic Systems for Benzyl Alcohol Oxidation

2.1.3.1 Various Non-Noble Metal-Based Heterogeneous Catalysts for Benzyl Alcohol Oxidation

Similar to the selective oxidation of common alcohols, various non-noble transition metal-based catalysts have shown activity in the transformation of benzyl alcohol such as Co_3O_4 [57] while the most extensively studied are those based on noble metals, including silver, ruthenium [58, 59], gold[60-62], platinum, and most importantly, palladium [62-67].

Silver supported on hydrotalcite (HT, $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$) has been employed by Mitsudome to selective oxidize benzyl alcohol under oxidant- and additive-free conditions [68]. Different from most catalytic procedures usually involving various oxidants, it can selectively convert benzyl alcohol into benzaldehyde with benzyl benzoate as byproduct through a dehydrogenation step. Besides the avoidance of

deactivation of catalysts by water and subsequent purification, another point worth noting is the coproduction of hydrogen, which is a very important type of new energy. Silver supported on different metal oxides have also been prepared and investigated for benzyl alcohol oxidation. Using a screening approach, Beier discovered the collaborative effect between ceria oxide and silver impregnated on silica. Not only the silver loading, the ratio of ceria oxide to silica, but also the calcination temperature has a profound influence on the activity of silver catalysts during the transformation of benzyl alcohol. However, different from the aforementioned Ag/HT system, the activated oxygen attributed to the presence of ceria can readily react with the hydrogen produced by silver catalysts impregnated on silica under a dehydrogenation route during benzyl alcohol transformation, resulting in the regeneration of silver surface [69, 70]. Also, to obtain good selectivity as well as high yields, the silver loading of is comparably high.

2.1.3.2 Various Noble Metal-Based Heterogeneous Catalysts for Benzyl Alcohol Oxidation

Besides silver, ruthenium is also applicable to benzyl alcohol oxidation. Ruthenium supported on hydroxyapatite, alumina, silica, iron oxide and carbon nanotubes have showed good activity in benzyl alcohol transformation. Different solvents such as toluene, trifluorotoluene, water or its mixtures, and oxygen pressure can play a vital rule. For example, ruthenium supported on $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ was successfully prepared by a cation-exchange procedure and can selectively oxidize benzyl alcohol into benzaldehyde with a turnover number of 290 in 24 hours [71]. Further studies confirmed the reaction undergoes a β -hydride elimination step after the ligand exchange between

Ru catalysts and benzyl alcohol and the catalysts can be recovered through the oxidation of Ru-hydride produced and subsequent ligand exchange. Common metal oxides, such as alumina can also be used as a support material. Ruthenium supported on alumina showed the highest activity compared to ruthenium compounds such as $\text{Ru}(\text{OH})_3 \cdot n\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, $[\text{RuCl}_2(\text{PPh}_3)_3]_2$, $[\text{RuCl}_2(\text{p-cymene})]$ and RuO_2 [72]. The mechanism involved can be represented by Figure. 3. A kinetic study showed that the β elimination step is the rate-limiting step. Similar mechanism can be applied to $\text{Ru}(\text{OH})_x/\text{Fe}_3\text{O}_4$ catalysts, the support of which makes separation and recycle of the catalysts more easily [73].

Figure 2.2 A mechanistic scheme of Ru/Alumina for benzyl alcohol oxidation [72].

Excellent activity, selectivity and stability of ruthenium catalysts supported on carbon nanotubes were also reported. The effect of solvents on the selective oxidation

of benzyl alcohol was carefully studied, with a toluene/water volume ratio equal to 2:1 having the best yields of benzaldehyde compared to other systems. This phenomena can be attributed to a better solubility of aldehyde in toluene as well as worse solubility in water than those of alcohol, which prevents further oxidation to acids [74].

A third one is gold-based heterogeneous catalysts. Fang et al has successfully prepared gold catalysts with controlled size supported on different supporting materials and studied their activity in oxidant-free benzyl alcohol dehydrogenation [75]. Results indicate the acid-base properties of these supports play an important role in both activity and selectivity of benzaldehyde. Gold supported on those with neither acidic nor basic sites have almost no activity and poor benzaldehyde selectivity, such as Au/SiO₂ and Au/La₂O₃; those with both have a high activity and excellent benzaldehyde selectivity, like Au/hydrotalcite; those with only one kind have a medium value, like Au/Al₂O₃, Au/MgO. Apart from the influence of acid-base properties of support materials, they also investigated the size effect of gold catalysts. They found that the conversion of benzyl alcohol increases with decreasing the gold nanoparticle size while the selectivity of benzaldehyde is kept unchanged. Such behavior can be attributed to the increase of ratio of coordinatively unsaturated gold numbers to saturated ones. Therefore, we can control the reaction process by choosing or synthesizing support materials with appropriate acid-base properties for different purposes. Usually, in aerobic oxidation processes, bases like sodium hydroxide or potassium carbonate are added to the reaction system due to their ability to improve the reaction rate by facilitating the oxidative dehydrogenation step [76]. In these catalytic systems, over-oxidation to benzoic acid or benzyl benzoate in aqueous media are often inevitable [76-78]. However, by changing

the solvents, high selectivity to benzaldehyde can be obtained. Buonerba found the use of chloroform and water ($v/v = 1:1$) as solvent can transform benzyl alcohol into benzaldehyde in high activity with excellent selectivity by Au/polymer catalysts they prepared. They attribute this phenome to the relatively low reaction temperature and the hydrophobic nature of the support material [79]. Besides the liquid phase oxidation systems, Zheng et al investigated the effect of bases on the solvent-free selective oxidation of benzyl alcohols. A trace amount of bases including metal carbonate, acetate or borate can also significantly improve the activity of gold catalysts due to their role as promoters [80].

Last but not least, palladium-based catalysts supported on different materials have also shown superior activity in benzyl alcohol oxidation. Compared to aforesaid systems based on various transition metals, the effect of supports are more profound. Mori et al compared the activity of palladium catalysts deposited on different supporting materials and found that those supported on hydroxyapatite with a formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ or HAP-0 can transform benzyl alcohol into benzaldehyde with almost complete conversion and selectivity while those supported on a calcium deficient hydroxyapatite $\text{Ca}_9(\text{HPO}_4)(\text{PO}_5)(\text{OH})$ or HAP-1 have no activity. Further evidence was showed when palladium supported on carbon, alumina and silica are employed, either with low conversion or low selectivity or both. Beside, solvents can also play a vital role. Pd/HAP-0 have no activity when aprotic solvents are used due to the inhibition of palladium reduction in the presence of heteroatoms. Trifluorotoluene is more effective compared to 1,2-diethoxyethane, the use of which causes lower conversion and worse selectivity [63]. Similar phenomena can be seen for palladium supported on activated

carbon or carbon nanotubes catalysts [81]. Zhou et al has studied the effect of solvents on the preparation of palladium supported catalysts. DMF can be used to prepare palladium nanoparticles with smaller particle size and broader size distribution on a new covalent-organic polymer, COP-4, which results in better activity with worse selectivity for the oxidation of benzyl alcohol compared to the counterparts prepared with distiller water [82]. Another important factor is the particle size. Chen et al has investigated the size effect on the activity of palladium for benzyl alcohol oxidation. They found that catalysts with a mean particle size about 3.6 nm have the best activity as well as selectivity to aldehydes and they ascribe this difference to structure sensitivity of palladium catalysts, similar to gold catalytic systems [66].

In conclusion, for selective oxidation of benzyl alcohol reactions based on noble-metal heterogeneous catalyst, the particle size, supporting materials, the solvent systems as well reaction temperature can have a profound influence in the activity as well as the selectivity. For particle size effect, the structure sensitivity effect can be attributed to the fact that coordinatively unsaturated atoms like corner atoms and face atoms are the ones that directly make contact and react with the substrate. Therefore, the relative abundance of them determines the activity of the catalysts. For the supporting materials effect, acidic and basic sites can act as promoters to be involved into the reaction. Appropriate solvents can separate the products from the catalysts, thus preventing the deactivation of the catalysts.

2.1.4 Heterogeneous Catalytic Systems for Ethyl Alcohol Oxidation

In the global attempt to reduce carbon footprint, the chemical and petrochemical industry face the problem to replace the currently used fossil feedstocks with renewable

resources. Alcohols such as ethanol can be produced on an industrial scale from biomass resources and it becomes a promising raw material that can be converted to value-added chemicals worth more interest, such as acetaldehyde, ethylene, ethyl acetate, ethane, diethyl ether, carbon monoxide/hydrogen, acetic acid *and* ethylene oxide, according the degree of oxidation. In ethanol selective oxidation reactions, transition metal oxides (such as vanadium, molybdenum, tungsten and nickel), noble metal-based materials (such as gold, platinum, palladium, silver, copper, ruthenium), zeolites (such as HY, ZSM-5, MOR, H β), octahedral molecular sieves have been widely studied.

2.1.4.1 Various Non-Noble Metal-Based Heterogeneous Catalysts for Ethyl Alcohol Oxidation

Transition metals, such as vanadium, molybdenum and tungsten have been reported as highly active catalysts in ethanol oxidation.

There have been a lot of studies on the catalytic performance of supported vanadia for the ethanol oxidation to acetaldehyde or acetic acid, which have shown to be dependent on the nature of the support. With supports such as Al₂O₃, Al₂O₃-ZrO₂, TiO₂, TiO₂/SiO₂, and ZrO₂-SiO₂, acetaldehyde is observed as the primary product, while acetic acid is observed at higher temperatures and conversions. However, when the support material was changed to MCM-41, the results are different. In 2006, Dogu reported that V-incorporated MCM-41 catalysts showed very high activity and high selectivity in the production of ethylene from ethanol in an oxidative process [83]. More interestingly, with the increase of temperature over 300 °C, ethylene selectivity increased significantly. The V/Si ratio also have a great influence on ethylene yield, the optimum of which was 0.04. On the other hand, relatively high acetaldehyde selectivity

were observed below 300 °C. Also, in the absence of gas-phase oxygen, acetaldehyde instead of ethylene was formed.

For molybdenum, less attention has been paid on ethanol oxidation than methanol oxidation, which has been extensively studied since the 1960s. As the same as vanadium, the nature of support has a significant influence on the catalytic activity of molybdenum. In 1995, Oyama investigated the oxidation of ethanol on MoO₃ supported on Al₂O₃, TiO₂, and SiO₂, with the reactivity sequence in the order: MoO₃/TiO₂>MoO₃/Al₂O₃>MoO₃>SiO₂ [84]. For all the catalysts, ethanol oxidation products are mainly acetaldehyde, diethyl ether and ethylene. He also pointed that although rates were strongly affected by the support, the rates did not depend substantially on the loading, which is due to a compensation between the equilibrated adsorption of ethanol and the rate-determining decomposition of the ethoxide intermediates.

Apart from vanadium and molybdenum, tungsten oxide-based catalysts have also been applied in the selective oxidation of ethanol. Dogu reported that their synthesized mesoporous solid acid catalysts composed of WO_x nanorods and W nanoballs within an amorphous silicate lattice have a very high activity for the simultaneous production of ethylene and diethyl ether [85].

In 2001, Baertsch proposed mechanisms for the formation of acetaldehyde and diethyl ether from ethanol over alumina-supported tungsten, vanadium and molybdenum oxides using in situ X-ray adsorption, diffuse reflectance infra-red Fourier transform spectroscopy and UV-visible spectroscopy[86]. Isotopic labeling shows that acetaldehyde formation from ethanol over VO_x, MoO_x and WO_x catalysts occurs via

rate-determining C-H bond cleavage of the CH₂ group in an adsorbed alkoxide followed by removal of surface oxygen in a Mars and van Krevelen redox mechanism; diethyl ether formation occurs in parallel via coupling and condensation of two adjacent ethoxy species. In detail, the first step for both acetaldehyde and ether formation is the adsorption of ethanol as an ethoxy species. The next step in acetaldehyde formation is the rate-determining abstraction of an H atom from the ethoxy species and concurrent reduction of the catalyst surface via removal of a redox-active bridging lattice oxygen in a Mars-van Krevelen redox mechanism. The catalyst is then immediately reoxidized using oxygen from the gas phase. For diethyl ether formation, the mechanism involves an S_N2 reaction between two adsorbed ethoxy species.

When vanadium and molybdenum are combined together, the catalytic activity of the new material may show some differences. Iglesia reported the direct oxidation of ethanol into acetic acid by the multiple component metal oxides Mo-V-NbO_x in the presence of colloidal TiO₂ with selectivities as high as ~95% even at 100% ethanol conversion [87]. Similar results are found on MoVNbTe mixed oxides catalysts [88].

2.1.4.2 Various Noble Metal-Based Heterogeneous Catalysts for Ethyl Alcohol Oxidation

For noble metals, Au is the most extensively investigated catalyst for ethanol oxidation [89, 90]. In 2006, Christensen reported for the first time that gold catalysts supported on MgAl₂O₄ for aqueous-phase oxidation of ethanol with air into acetic acid at 374-473 K with O₂ pressure of 0.5-1 MPa [91]. He then compared the performance of Au/ MgAl₂O₄ and Au/TiO₂, which showed that these two catalysts exhibited similar performance in the reaction of ethanol oxidation [90]. Underlining these interesting

results are the reaction pathway: ethanol is first absorbed to the catalysts surface, resulting in forming an activated intermediate species; then the intermediate species are oxidized/dehydrogenated to the aldehyde; finally, the aldehyde is further oxidized to the acid. By varying the amount of water in the reaction mixture, ethyl acetate can also be produced. Typically, ethyl acetate involves the esterification of acetic acid, during which water has played an important role. In conclusion, the product selectivity over Au catalyst is sensitive to the ethanol concentration: at low ethanol concentrations, the primary product is acetic acid; when the ethanol concentration is greater than 60 wt%, the product is then mainly ethyl acetate [90, 91].

In 2008, Mullins reported the results of the oxidative conversion of ethanol into acetaldehyde on Au(111), which involves that ethanol initially undergoes O-H bond cleavage (producing ethoxide) followed by selective β -C-H bond activation to form acetaldehyde and water on atomic oxygen precovered Au(111) [92]. Friend thoroughly investigated the mechanism for the ethanol oxidation on O-covered Au(111) in 2009. He demonstrated that the concentration of adsorbed oxygen plays a vital role in controlling reaction selectivity: for an initial O concentration of ~ 0.05 ML, ethanol oxidation produces ethyl acetate predominantly and ester yields in maximum at an initial O coverage of ~ 0.2 ML; at higher initial oxygen coverages, secondary oxidation to acetic acid, ketene, and CO_2 increases at the expense of ester formation [93]. He explained that oxygen is required for ethoxy formation and following steps, while there is no measurable reactions on clean Au(111). As ethoxy is converted into acetaldehyde, two pathways compete: esterification via direct attack of the aldehyde by ethoxy and oxidation to acetate, the relative contributions of which depend strongly on the oxygen

coverage, with moderate coverages yielding both ester formation and secondary oxidation [93].

During oxidation reactions, noble metallic catalyst nanoparticles' sizes and their size distributions play important roles in influencing the catalytic activity for the reactions, and have therefore been studied extensively in recent years. Hensen has demonstrated that a strong influence of the gold particle size on the non-oxidative dehydrogenation of ethanol is noted: gold nanoparticles of about 6 nm show a much higher activity than smaller or larger particles. He attributed the optical catalytic activity to the existence of surface steps with a suitable geometry for the removal of β -H atoms from adsorbed ethoxide. Such stepped sites are expected to be present with maximum density for intermediate particle size [94].

In addition to the size effect of metal nanoparticles, the nature of support material is also identified as a crucial factor to influence the catalytic activity of primary active sites [95]. Sobolev investigated gas-phase oxidation of ethanol over gold catalysts supported on titania, alumina and silica. Different from the other two, Au/TiO₂ can catalyse ethanol into acetaldehyde at usually low temperature, around 125 °C. Compared with gold supported on Al₂O₃ and SiO₂, which showed usual catalytic behaviour with a steady increase of ethanol conversion above 200 °C, this catalyst showed two peaks of activity, suggesting different pathways may exist in ethanol oxidation at different temperatures for Au/TiO₂ [96].

Apart from gold catalysts, over noble metal-based materials, like platinum, palladium, silver, copper, ruthenium, have also been extensively studied in the selective oxidation of ethanol.

About two centuries ago, for the first time, Dobereiner discovered that platinum can oxidize ethanol into acetic acid by air. Since then, a lot of scientists have been devoting to uncover the magic power of this noble metal. For example, Marin investigated oxidative dehydrogenation of aqueous ethanol into acetaldehyde and acetic acid on a carbon supported platinum catalysts. By analysing the concentration vs. space time curve of the reaction, he proved that the oxidation proceeds by a sequence in which acetaldehyde and acetic acid are formed successively [97]. Wang investigated the partial oxidation of ethanol for hydrogen production over three types of supported platinum catalysts: Pt/Al₂O₃, Pt/ZnO, Pt/ZrO₂, with the major productions H₂, H₂O, CO and CO₂. By comparison, he pointed that Pt/ ZrO₂ was an excellent catalyst for selective and effective production of hydrogen at a low temperature, with the selectivity for CO approaching zero and the selectivity for H₂ no less than 90% at 370K [98]. Many researchers also applied platinum based catalysts to ethanol electro-oxidation. Lamy investigated the catalytic performance of ethanol electro-oxidation over Pt, Pt-Sn, Pt-Re dispersed on a high surface area carbon powder with acetaldehyde, acetic acid and carbon dioxide as the main products during electrolysis [99]. Chen compared the performance of Pt/C and that of Pd/C in alkaline media for ethanol electro-oxidation, in which the effects of ethanol concentration, NaOH concentration as well as temperature were thoroughly studied [100].

Besides gold- and platinum-based catalysts, palladium also plays a crucial role in ethanol selective oxidation. In the reaction, supported Pd catalyst can transform ethanol into acetic acid, which then can be further catalytically esterified to ethyl acetate by the protons dissociated from acetic acid. Chang investigated the difference of the catalytic

performance between hydrophilic and hydrophobic Pd catalysts, taking styrene-divinylbenzene copolymer (SDB)-supported Pd catalyst and γ -alumina-supported Pd catalyst as examples for the two types, respectively. In his study, he found that because of capillary condensation, the ethanol conversion catalysed by Pd/SDB is much higher than that catalysed by Pd/ γ -Al₂O₃ [101]. Using first-principle density functional theory, Neurock studied the influence of oxygen and pH on the selective oxidation of ethanol over a model Pd(111) surface. He concluded that O₂ plays a role as removing the electrons produced in the oxidation reaction via the oxygen reduction reaction over Pd [102]. Gusevskaya reported selective direct synthesis of symmetric acetals using a chloride-free Pd(OAc)₂/Cu(OAc)₂/p-TsOH system as an efficient bifunctional catalysts [103]. There are also numerous reports focused on electro-oxidation of ethanol using Pd based catalysts [100, 104].

Because of the low production and expensive prices of Au, Pt, Pd, many researchers tend to use much cheaper alternatives, like copper and silver. Copper-based catalysts have been successfully employed for the selective oxidation of ethanol to ethyl acetate and acetaldehyde. Al₂O₃, SiO₂, ZrO₂, carbon nanotubes, MCM-41 are widely used as the support material of the catalysts. Bueno investigated the influence of active sites for ethanol oxidation over Cu/SiO₂, CuO/SiO₂ and Cu/ZrO₂ catalysts. He found that the Cu⁺¹ provided by the CuO/SiO₂ was highly selective for the dehydrogenation of ethanol, while the Cu⁺¹/Cu⁰ pair provided by CuO/SiO₂ generated sites of very low selectivity for ethyl acetate and high selectivity for acetaldehyde. The efficient direct transformation of ethanol into ethyl acetate requires a combination of the Cu⁺¹/Cu⁰ pair and high electron density Cu⁰ chemically interfaced to ZrO₂ [105]. Velu reported partial

oxidation of ethanol into acetaldehyde over Cu/MCM-41 catalysts with a good selectivity. Interestingly, with increasing copper content, the activity for ethanol conversion also increased; the presence of Zn^{2+} can also promote the catalysts' activity [106]. Schneider studied the catalytic performance of $[\text{Cu}_2\text{O}/\text{MWCNT}]$ and $[\text{Cu}_2\text{O}/\text{ZnO}/\text{MWCNT}]$ for selective partial oxidation of ethanol to acetaldehyde with molecular oxygen. When using binary catalyst, acetaldehyde was obtained with a yields of 87% at 355 °C with selectivity 96% and conversion 91%,; while using ternary composite, the products are mainly hydrogen and carbon dioxide due to the fact that dehydrogenation and total oxidation pathways is more favoured compared to the binary composite [107]. Copper-based catalysts can also transform ethanol into ethylene oxide and acetone. Lippits thoroughly investigated the performance of alumina supported copper catalysts in ethanol oxidation: pure support, that is Al_2O_3 in our case, produces diethyl ether and ethylene only; addition of copper results in a direct conversion of ethanol into ethylene oxide; further addition of Li_2O can suppress the formation of diethyle ether and ethylene, which can improve the selectivity to ethylene oxide greatly [108]. Bussi reported the gas phase conversion of ethanol-water mixtures into acetone using copper-pyrochlore catalysis, the maximum yields of which can be 96% of the stoichiometric amount at 400 °C [109]. He attributed this performance to the acid-base properties of $\text{La}_2\text{Zr}_2\text{O}_7$, its higher specific surface area and copper dispersion. At last, he pointed the possible mechanism: ethanol dehydrogenation to acetaldehyde followed by oxidation to acetic acid and further ketonisation to acetone.

Although silver is not studied as much as other noble metals, there have been some reports involving its catalytic activity in ethanol oxidation. Lippits reported that addition

of silver nanoparticles promotes the conversion of ethanol into ethylene oxide, while diethyl ether and ethylene are the only products without the addition. Further addition of Li_2O can improve the selectivity to ethylene oxide of the catalysts, while addition of Ce_xO results in the production of CO [108]. Vodyankina reported that Ag-containing Si_3N_4 catalysts have high selectivity/activity in ethanol oxidation (95% acetaldehyde selectivity and 100% ethanol conversion at 300 °C [110]. Shen also reported that Ag-hollandite nanofibers can selectively oxidize ethanol to acetaldehyde with a conversion of 82% and selectivity of 95% at 503 K for 120 h time-on-stream [111].

Last not the least, ruthenium has begun attracted much attention in the selective oxidation of ethanol due to its inner chemical properties. Riisager thoroughly investigated the activity of ruthenium hydroxide supported on titania, alumina, ceria and spinel in term of Ru metal loadings, pretreatment of catalysis, oxidant pressure, reaction temperature and substrate concentration. Ethanol can be selectively and efficiently oxidized into acetic acid with the catalysts at a temperature between 125 °C and 200 °C and elevated oxygen pressure. There is no significant change on the yields when the substrate concentration varies between 2.5-50 wt%. The performance of catalysts increased in the order: $\text{Ru(OH)}_x/\text{TiO}_2 < \text{Ru(OH)}_x/\text{Al}_2\text{O}_3 < \text{Ru(OH)}_x/\text{MgAl}_2\text{O}_4 < \text{Ru(OH)}_x/\text{CeO}_2$ when other conditions are the same with each other [112]. Iglesia studied RuO_2 domains supported on SiO_2 and SiO_2 for ethanol selective oxidation. $\text{RuO}_2/\text{SiO}_2$ and $\text{RuO}_2/\text{SiO}_2$ can convert ethanol- O_2 reactant mixtures with high rates and selectivity to form acetaldehyde, diethoxyethane, and ethyl acetate at 393 K. In the reaction, ethanol pressure has a great impact on ethanol conversion rate and the products. Ethanol conversion rates increased with pressure and then reached a constant value. As

ethanol pressure increased from 2 to 40 KPa, products shifted from acetaldehyde (97.3 to 17.6%) to diethoxyethane (0 to 81%). Underling the reaction is the mechanism: initial oxidative dehydrogenation of ethanol to form acetaldehyde and subsequent acetalization reactions of acetaldehyde and ethanol to form diethoxyethane [113].

The discussion above is mainly focused on monometallic catalysts, however, bimetallic or trimetallic catalysts may also be very effective in the ethanol selective oxidation. Wang synthesized and investigated the catalytic performance of Rh/Pt bimetallic ultrathin nanowires, which displayed electrocatalytic performance and at least 2.69 times higher selectivity to CO₂ compared with the commercial Pt black thanks to the effective ability of Rh [114]. Remita successfully synthesized gold-rich core and Pd porous shell alloy nanoparticles using hexagonal mesophases as a template and found that the catalysts exhibit a very good electrocatalytic activity and high stability for the oxidation of ethanol [115]. Dai developed Au-CuO_x hybrid catalysts by oxidative dealloying silica-supported Au-Cu alloy nanoparticles and found that oxidation of the alloy at 300 °C produce the most active and stable catalyst for ethanol conversion (~90%) with highest selectivity (~80-90%) to acetaldehyde at a reaction temperature of 200 °C for 50h on-stream in the presence of oxygen while AuCu catalyst calcined at 500 °C showed the highest conversion in a He atmosphere [116]. Xu also reported that Au@Pd bimetallic and Pt-on-(Au@Pd) trimetallic nonastructures show high activity and fari stability in the ethnl electro-oxidation compared to conventional Pd black catalysts [117].

In conclusion, for ethanol oxidative dehydration, the oxide products are typically acetaldehyde, acetic acid, ethylene oxide, ethyl acetate, carbon monoxide, carbon

dioxide, and water. According to the last ten years' major work on ethanol transformation summarized by Takei et al. [118], acetaldehyde was the primary product of ethanol oxidation over transition metal oxide catalysts, such as Cu, V and Mo. For noble metals, Au is the most extensively investigated catalyst for ethanol oxidation to acetic acid, and acetic acid yield of 90–95% can be achieved at moderate temperatures and pressures. Platinum, palladium, silver, copper, ruthenium have also been widely studied and some of them show great potential in ethanol selective oxidation.

2.2 Introduction to Titanium Dioxide Materials

Titanium dioxide has been widely used in white pigment industry since Ford von Bichowsky developed an easy, iron-free and low-cost method to manufacture the so-called “titanium white” in the 1920s in large-scale [119]. Since then, its applications have been extended to whitener in toothpaste [120] and food coloring [121], UV absorber in sunscreens [122] and many other areas. But it was not until 1972 when Fujishima and Honda discovered its water-splitting ability under UV irradiation [123] that its power has been really re-examined. Due to its intrinsic and tunable photoelectric properties [124], titanium dioxide can be found applications in “energy” and “environmental” fields. Typical examples in the “energy” filed include ultra-violet induced hydrogen production from water [123, 125-128] and organic chemicals like ethanol [129]; reduction of carbon dioxide into organic compounds such as formic acid and formaldehyde [130, 131], methane and methanol [132-136], acetic acid and alcohols [137], carbon monoxide [138] and many others [139-143]; safer anode material for lithium rechargeable batteries/supercapacitors [144, 145]. Besides, it can also be used in photovoltaic devices which convert solar energy into electricity power [146].

Based on the modifications, such devices involved titanium dioxide can be roughly divide into these categories: dye-sensitized solar cells [147], polymer-inorganic hybrid solar cells [148-150], quantum dot-sensitized solar cells [151-153], inorganic solid-state solar cells [154, 155], perovskite solar cells [156, 157] and so on. Being inexpensive, nontoxic, highly stable chemically and optically, corrosion resistant, environmentally friendly [158], titanium dioxide can also be used in the “environmental” filed. Photocatalytic decomposition of organic pollutants such as chloroform [159], carbon tetrachloride [160], 2-propanol, phenol, 4-chlorophenol, pentachlorophenol [161, 162] as well as organic dyes [163] show its powerful abilities in air, water and soil purification. Another important application in the environmental filed is the titanium dioxide-based sensors. On account of different sensing targets or measurement principles, these devices can be grouped into three categories: gas sensors, chemical oxygen demand (COD) sensor and biosensor [164]. Gas sensors, including hydrogen sensor [165, 166], oxygen sensor [167], humidity sensor [168, 169], carbon monoxide sensor [170-177], volatile organic compounds sensor [178-181] and sensors for other gases [182], have shown superior gas sensing performance as well as excellent applied prospect [164]. According to different photocatalytic oxidative methods, titanium dioxide COD sensors can be further classified into photocatalytic COD sensor [183, 184] which is based on tracing of dissolved oxygen or metal ions concentration[164] and photoelectrocatalytic COD sensor [185, 186] which relies on photocurrent measurement[164]. Due to nontoxicity and excellent biocompatibility, titanium dioxide can also be applied to biosensors. Typical examples are amperometry biosensor [187], potentiometry biosensor [188], and optical radiation biosensor [189, 190].

Despite the aforementioned applications in the later developed functional as well as conventional areas, titanium dioxide can also be utilized to the classical catalysis field, mostly as support material for noble metal catalysts. For example, gold supported on titanium dioxide has been extensively studied in carbon monoxide oxidation both theoretically [191] and experimentally [192-194] due to its relative simplicity as a model reaction as well as importance in pollution remediation. Another utilization of titanium dioxide supported gold catalysts is the removal of carbon monoxide from hydrogen-rich feed streams for low temperature fuel cells [195]. Other noble metal elements such as palladium [196] supported on titanium dioxide also demonstrate excellent ability in carbon monoxide oxidation. Hutchings discovered apart from the particle size, catalyst and support interaction, the ratio of gold and palladium can have a profound impact on the conversion as well as the selectivity of alcohol oxidations [197].

According to Zhang's report [198], there are at least eleven bulk and/or nanocrystalline phases of titanium dioxide, among which rutile, anatase and brookite are the main phase structures found in nature. Typically, brookite is the least stable phase among them while rutile is more stable at most temperatures and pressures [164], or thermodynamically stable phase. In contrast, anatase is stable under mild conditions. However, when applied to heat treatment between 600-700 °C, phase transformation from anatase to rutile occurs. Some of the structural characteristics of the main three titanium dioxide phases are summarized in Table 1.

Table 2.1 Structural characteristics of the main three titanium dioxide crystalline phases [198].

Phase	Crystal system	Space group	group	a (Å)	b (Å)	c (Å)	density ^a g/cm ³	Ref.
rutile	tetragonal	<i>P4₂/mm</i>	136	4.5941	4.5941	2.9589	4.248	ICSD #9161
anatase	tetragonal	<i>I4₁/amd</i>	141	3.7842	3.7842	9.5146	3.895	COD#9008213
brookite	orthorhombic	<i>Pbca</i>	61	9.184	5.447	5.145	4.123	ICSD #15409

^aCalculated.

2.3 Various Carbon Nanomaterials

The unique ability of carbon to form covalent bonds with other carbon atoms in various hybridization ways predestines them to form a wide range of structures, from the simplest organic molecule methane with four hydrogen atoms attached to one carbon atom covalently, to supermolecules with hundreds of thousands of carbon atoms and many others. Among them, one of the most fascinating and well-received area in modern chemistry and material science is the one based on carbon nanomaterials. Following the discovery of the first of these interesting materials C₆₀ in 1985 by Kroto[199], Iijima reported the existence of multi-walled carbon nanotubes (MWCNT) while synthesizing C₆₀ and other fullerenes using an arc-discharge evaporation method in 1991[200]. About two years later, another form of carbon nanotube, namely, the single-walled carbon nanotube (SWCNT) was discovered [201]. Until now, other carbon-based nanostructures, including nanofibers[202-205], single-walled carbon nanohorns (SWNHs)[206], onion-like carbon (OLC) spheres[207, 208], bamboo-like nanotubes[209], graphene[210-212], carbon dots[213], graphene quantum dots[214], nanodiamonds[215, 216], graphene nanoribbons[217, 218], have greatly enriched the family of carbon-based nanomaterials.

Based on the dimensionality, these nanostructures can be categorized into zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) materials. Fullerenes, onion-like carbon structures, carbon dots, graphene quantum dots and nanodiamonds are typical examples of 0D nanomaterials; while carbon nanotubes, carbon nanofibers, and single-walled nanohorns belong to the 1D nanostructures. 2D nanomaterials mainly consist of graphene and its derivatives, such as graphene nanoribbons and few-layer graphenes. 3D nanostructures include graphite and diamond. Another approach to classify these materials is on the basis of the type of hybridization state of carbon atoms in these structures. Fullerenes, carbon nanotubes, nanohorns, onion-like carbon spheres, carbon dots, graphene and its derivatives can be grouped into graphenic nanostructures with most of the carbon atoms are covalently bonded with another in sp^2 states. The rest, consisting mostly sp^3 carbons or with sp^2 and sp^3 carbon atoms in different ratios can be categorized into the diamondic group, with nanodiamonds the only example until now [219]. A third way of classifying these materials is based on whether they have empty internal spaces. The internal voids of

fullerenes, carbon nanotubes, nanohorns can be used to capture gas, small organic molecules, even small nanostructures, while the rest cannot.

Figure 2.3 Classification of various carbon nanomaterials according to their dimensionality [219].

2.3.1 Physical and Chemical Properties of Carbon Nanotubes

Based on the number of graphenic layers in a nanotube, carbon nanotubes can be categorized into single-walled carbon nanotube (SWCNT), double-walled carbon nanotube (DWCNT), and multi-walled carbon nanotube (MWCNT). As mentioned in

Table 1, the diameter of a carbon nanotube can be as tiny as 0.4-2 nm for SWCNT, several tens even more than one hundred of nanometers for MWCNT. The length can also be very different, ranging from less than one hundred nanometer to several micrometers depending on the synthesis methods and post-synthesis modifications [220]. But the aspect ratio (the ratio of length to diameter) frequently exceeds 10000[219], which is far much larger than its nanoallotropes. Except for the number of layers and length of a nanotube, the third important factor to influence its physical and chemical properties is chirality, the chiral angle between hexagons and the tube axis [221]. Based on the chirality, multi-walled carbon nanotubes can be formed in several ways, with zigzag, armchair and chiral the most common examples [219]. Different from C_{60} , carbon nanotubes neither dissolves in organic solvents nor inorganic solvents like water. Usually, techniques such as ultrasonication are applied to disperse them in various solvents; however, it will precipitate again once the applied force is removed.

Figure 2.4 Three typical ways of graphene wrapping along the tube axis [222] and the resulting structures (a) armchair (b) zigzag (c) chiral [223].

It has been both theoretically predicted and experimentally measured, carbon nanotubes have high Young's modulus and tensile strength. Thus, carbon nanotubes can be used to enhance the mechanical strength of composite materials. Besides, similar to graphite and diamond, carbon nanotubes also have low heat capacity and high thermal conductivity [224]. More importantly, carbon nanotubes are widely used as a supporting material due to its high thermal stability, large surface area and tubular characters.

2.3.2 Synthesis of Carbon Nanotubes

Inherited from the synthesis of fullerene, carbon nanotubes were first synthesized by the arc discharge method [200]. Until now, many other approaches have been applied to obtain high yields, high quality, low-cost and impurity-free carbon nanotubes. These methods mainly include arc discharge, laser ablation, sono-chemical or hydrothermal, electrolysis and chemical vapor deposition [225]. Single-walled carbon nanotubes, double-walled carbon nanotubes, or multi-walled nanotubes can be prepared with different physical and chemical properties as well as different crystallinity and extents of purities depending on the synthesis methods and parameters of the synthesized condition.

Arc discharge can be used to prepare high-quality carbon nanotubes with nearly perfect nanostructures. It usually involves high temperatures, typically more than 1700 degree Celsius [225]. For multi-walled carbon nanotubes, DC arc charge are well-received with different supporting gases such as helium [200, 226], hydrogen or methane [227, 228], a mixed atmosphere of helium, ethanol, acetone and hexane [229] and ammonia [230]. The gas atmosphere, pressure and gap between the electrodes can influence the purity and yield of the products greatly. Apart from DC arc discharge,

single-pulse arc techniques are also studied to produce multi-walled carbon nanotubes [231]. Other non-standard arc-discharge techniques using liquid solutions instead of supporting gases are also proved feasible to obtain multi-walled carbon nanotubes. Typical examples are liquid nitrogen [232-234], H_3VO_4 aqueous solution [235] and water [234, 236].

Different from the preparation of multi-walled carbon nanotubes using arc discharge approach when no catalysts is needed, transition metal catalysts such as cobalt [201, 237, 238], nickel[239, 240], iron[241], or platinum group elements like palladium[239, 242], platinum[239, 242], rhodium[242] are necessary. Hydrogen or argon are usually used as the supporting gas [225].

Figure 2.5 Simple representation of the arc discharge apparatus for CNT synthesis[243].

A second way to prepare carbon nanotubes is laser ablation [244] which use a laser to directly hit a mixture of graphite composite and transition metal catalysts. Many factors including the laser source, the catalysts used and the properties of the buffer gas can significantly influence the products. Unlike the versatility of the arc discharge method to produce single-walled carbon nanotubes, double-walled carbon nanotubes and multi-walled carbon nanotubes, this method is more used to produce single-walled carbon nanotubes.

Figure 2.6 The laser ablation apparatus used by Smalley in CNT production [244].

The two aforementioned methods, arc discharge and laser ablation methods, are usually proceeded under high temperatures, normally thousands of degrees Celsius, due to the enormous amount of energy needed to vaporize the solid –state carbon sources [221]. Urged by the energy crisis nowadays, energy-saved methods such as chemical vapor deposition (CVD) are developed to be the standard method for CNTs production [225]. Among them, thermal chemical vapor deposition and plasma enhanced chemical vapor deposition, are becoming more and more popular to produce high-purity carbon

nanotubes. Within the proposed mechanisms of carbon nanotubes growth, the well-received model is Fotopoulos's base growth and subsequent tip growth hypothesis [225, 245], which involves the participation of transition metal or palladium as catalysts. Similar to arc discharge methods, cobalt[246-248], nickel[245, 249-252], iron[246, 253] or Co/Fe binary system[253-255] are the most utilized catalysts in chemical vapor deposition while the carbon sources used includes alkanes like methane[249, 250, 256], ethane[257], and isobutane[258], alkenes such as ethylene[259], alkynes including acetylene[260-262], aromatic hydrocarbons like benzene[248, 263] and xylene[264, 265]. Even ethanol [248, 266, 267] and dimethyl sulfide [268] can be used as the carbon source in chemical vapor deposition. Apart from the carbon sources, substrates can also play a vital role to obtain high-quality products. Nickel [269], silicon [262, 270, 271], mesoporous silica [249, 250, 253, 255], stainless steel [269] or glass[262, 270, 272], CaCO_3 [273], graphite foil[251, 274], tungsten foil[274], zeolites[254] are commonly used to be the substrate materials in chemical vapor deposition. Different from catalytic chemical vapor deposition method, plasma enhance chemical vapor deposition are more suitable to produce CNTs hybrid materials and modifications of their surface properties with functional groups such as oxygenated and aminated groups [225, 275].

Besides traditionally used catalytic chemical vapor deposition and plasma enhanced chemical vapor deposition, water assisted chemical vapor deposition [276-278], oxygen assisted chemical vapor deposition [279], hot-filament chemical vapor deposition [280], microwave plasma chemical vapor deposition [281] and radiofrequency chemical vapor deposition [282] are also proved to be viable routes to produce carbon nanotubes.

Some other non-standard techniques are also used to obtain carbon nanotubes. Liquid pyrolysis is one of them. Liquid hydrocarbons such as ethanol[283-285], toluene[286, 287], hexane[288], various pinene components[289], neem oil[290], coconut oil[291] and waste pyrolysis oil[284] can be used as the carbon source while solid catalysts like cobalt and molybdenum acetates[292], ferrocene[287, 288, 293] are proved to be effective to catalyze the reaction. Solid state pyrolysis [294-297], flame pyrolysis and bottom-up organic methods [298-300] also enriched the family of nonstandard approaches to synthesize carbon nanotubes.

2.3.3 Purification of Carbon Nanotubes

Similar to other carbon nanoallotropes like nanodiamonds, impurities are usually present with different extents according to the preparation methods; sometimes they can even significantly interfere the characteristic properties of the desired products when applied under test or post-synthesis usage [219]. Apart from the incompletely reacted carbon precursors, carbonaceous byproducts like amorphous carbon, fullerene, and carbon nanoparticles are the main impurities [301]. The influence of impurities becomes even more profound when transition metal particles such as cobalt, nickel, iron or binary systems are used as catalysts in the synthesis procedure. Therefore, purification methods are equivalent importance as the synthesis methods to obtain high quality, impurity-free carbon nanotubes. Until now, there is now one-step standard or normalized method to ensure the complete removal of all these impurities. However, we can make full use of the differences of chemical and physical properties of carbon nanotubes and its byproducts to separate them from each other and keep the morphology and structure of carbon nanotubes at the same time.

Physical approaches are more preferred mainly due to its ability to keep the structure of desired products and to remove metallic byproducts and other impurities. In theory, any difference in physical property can be used as long as it can give us the desired products. However, commonly used physical means are mostly based on solubility, density, electronic and thermal properties. For example, carbon nanotubes like fullerene and aromatic carbons can be readily dissolved in organic solvents like toluene and carbon disulfide [302] while carbon nanotubes cannot, so we can use this difference in solubility to separate them. Techniques like filtration [303-305] and centrifugation [306, 307] take advantage of the difference in physical size, density, gravity and aspect ratio. To make the process more efficiently, surfactants such as sodium dodecyl sulfate (SDS) or sonication are also necessary to disperse the crude products in the solution well. High temperature annealing under vacuum conditions [308-310] or in protective gases such as nitrogen [311], argon [312] can efficiently vaporize the metallic components in the as-prepared carbon nanotubes and leave the desired products undamaged. Sometimes, it can even improve its crystallinity [309, 310] and remove all the functional groups formed during the synthesis procedure. However, the carbonaceous parts are becoming more difficult to remove after graphitization [301]. So its application has been limited to carbon nanotubes with less carbonaceous byproducts or the carbon nanotubes should be removed before applying to heat treatment. Besides the aforementioned three techniques, chromatography [313-316] and electrophoresis [317-319] can also be used to remove the impurities. The former one is based on the difference of size and morphology of the components. Components larger than the pores used in the chromatography usually have a shorter distance and would be

flowing out earlier than the smaller parts. Therefore, not only carbon nanoparticles and carbon nanotubes can be separated, carbon nanotubes with different lengths can also be classified [320, 321]. The latter one is viable due to the difference of intrinsic electric properties of carbon nanotubes and impurities which results in motion rate differences when a direct (DC) or alternating (AC) current is applied. The size and morphology can also affect the mobility of them. Apart from the purification means described above, solubilization of carbon nanotubes with functional groups [322-328] and field-flow fractionation (FFF) [329, 330] can also be useful to remove impurities. Physical approaches like centrifugation, filtration, chromatography, electrophoresis, solubilization and field-flow fractionation can prevent the structural properties of carbon nanotubes from being damaged and remove some of the impurities simultaneously. However, they usually require a good dispersibility of the mixtures in the solvent and sometimes it is really time-consuming.

An alternative is the chemical approaches. To remove the carbonaceous components in the mixture, selective oxidation including gas phase oxidation, liquid phase oxidation and electrochemical oxidation are often applied, which is based on the facts that carbonaceous impurities usually have more defects or large curvature than the carbon nanotubes, resulting in the faster oxidation rate of them[301]. The oxidizing atmospheres are based on oxygen in air [331, 332] or a mixture of argon, oxygen and water [333-335], or a mixture of hydrosulfide and oxygen[336], even a mixture of oxygen, sulfur hexafluoride and 1,1,1,2-tetrafluoroethane[337], chlorine in a mixture of chlorine, water and hydrochloride[338]. As the synthesized carbon nanotubes are not “perfect” structures, to minimize the loss of desired products in the gas phase oxidation process,

an even expose of the mixture to the gases is preferred. Also, as a consequences, it usually results in cut carbon nanotubes with open-tip, sometimes even being functionalized. Compared to the gas phase oxidation which is usually proceeded under high temperatures, liquid phase oxidation is much milder and energy-saving; more importantly, the metallic components can also be removed at the same time. Therefore, no subsequent processes are needed. Typical liquid phase oxidation techniques include mild acids like nitric acid [339-341], a mixture of nitric acid and sulfuric acid [342-344], bases like sodium hydroxide. The metallic components can be readily reacted with the acids and washed away. Sometimes oxidants like hydro peroxide [345-347] and potassium permanganate [348-350] are often added to enhance the oxidizability and remove some of the carbonaceous parts like amorphous carbon. However, it is not capable of removing large graphite particles and the carbon nanotube walls are often functionalized with carboxylic groups after the purification process. Electrochemical oxidation is based on the different corrosion rates of the impurities and carbon nanotubes. Alkaline media such as KOH solution [351] or acidic media like hydrochloride, sulfuric acid [352], nitric acid or a mixture of them are often applied. Not only most of the carbonaceous impurities like amorphous carbon, graphite particles can be separated from the desired products, but also the metallic components can be easily removed.

In general, none of the physical or chemical techniques can efficiently remove all the impurities used alone. Mostly, they are combined together to separate most of the unwanted parts and the desired products while keep the structural properties of the

carbon nanotubes. Also, the advantages and disadvantages of each method should be carefully examined before being applied.

2.4 Zeolites as Support Material and Catalysts

In 1756, the Swedish mineralogist A. F. Cronstedt discovered that an unidentified silicate mineral fused readily in a blowpipe flame with marked intumescence after heat. This result led him to call minerals behaving in this manner zeolites, in which ‘zeo’ means ‘to boil’ and ‘lithos’ means stone in Greek [353]. Since then, many researchers have been devoting themselves to investigating these magic material. In 1896, Friedel proposed the idea of an open framework based on the observations that various liquids were retained by some dehydrated zeolites. In 1925, dehydrated chabazite was observed to adsorb water, alcohols and formic acid, but no acetone, ether or benzene, which is the first example of zeolites working as a molecular sieve. However, natural zeolites are of limited value, because (i) they almost always contain undesired impurity phases, (ii) their chemical composition varies from one deposit to another and even from one stratum to another in the same deposit, and (iii) nature did not optimize their properties for catalytic reactions [354]. So the synthesis of fixed composition, highly active zeolites became more and more important to make full use of them. It was not until in 1948 Barrer and coworkers successfully prepared the first synthetic zeolites [355]. Since then, various kinds of zeolites including ZSM-5, Zeolite-A, X and Y have been synthesized for different purposes.

Initially, the commercial use of these zeolites were mainly for drying gas and refrigerants, but the industrial use of zeolites as catalysts in petrochemical processes greatly inspired its potential. Firstly, at the beginning of the 1960s, zeolites replaced

amorphous aluminosilicates as cracking catalysts. Soon, Metal doped Y-zeolites proved successful as bifunctional catalysts in the field of hydrocracking. The discovery of ZSM-5, the first representative of the family of pentasil zeolite, was a milestone in zeolite chemistry during the 1970s; the use of silicon-rich pentasil zeolites as highly acidic, extremely shape-selective and heat-stable catalysts led to new industrial petrochemical processes: selectoforming, olefin oligomerization, dewaxing and the MTG (methanol to gasoline) process have established themselves as industrial processes alongside cracking and hydrocracking. The catalysts were also used in selective reactions such as the Mobil-Badger process for alkylation of arenes, the *para*-directed isomerization of xylenes and the disproportionation or alkylation of monosubstituted arenes.

Underpinning all these applications are the well-defined pore structure, high thermostability and remarkable acidic properties of zeolites.

Well-defined pore structure are originated from the complex building blocks of zeolites. In zeolites, the fundamental building block is a tetrahedron, in which four oxygen anions surround a small silicon or aluminum ion and each apical oxygen atom is shared between two adjacent silica or alumina tetrahedron. The silica and alumina tetrahedral are combined into more complicated secondary units, which form the building blocks of the framework of crystal structures. The tetrahedral are arranged so that the zeolites have an open framework structure which defines a pore structure with a high surface area, mainly channels, interconnected voids or cages. It is these pores that exerts a steric influence on the reaction, controlling the access of reactants and products.

The silica and alumina tetrahedral are geometrically arranged, with Al-O-Al bonds excluded. The unit cell formula is usually written as

where A is a cation with the charge m, (x+y) is the number of tetrahedral per crystallographic unit cell and x/y is the so-called framework silicon/aluminum ratio n_{Si}/n_{Al} (or simply Si/Al) [354]. These metal cations, that is A in the formula above, are usually alkaline earth metal and alkali metal cations and some of them must be reversibly ion exchangeable to be classed as zeolites. Water and other small molecules always fill the channels, cages and interconnected voids.

Research showed that the thermostability and acidity of zeolites are closely dependent on their Si/Al ratio. The stability of the crystal framework increases with decreasing aluminum content resulting the deposition temperatures range from 700 °C to 1300 °C.

In principle, the exchangeable cations should be placed near alumina tetrahedral in order to cancel the negative charges caused by equivalent chemical values of aluminum and silica. However, in the actual zeolite, the negative charge is not localized on one or two tetrahedral but is mobile within the framework of oxygen ions. The mobility of exchangeable cations may play an important role in catalysis reactions.

In the synthesis of zeolites, alkaline earth metal and alkali metal cations are usually used to balance the framework charges caused by aluminium and these cations can be readily exchanged for protons by direct reaction with an acid, giving surface hydroxyl groups- the bronsted sites. (In chemistry, different from a Lewis acid, which is defined

as an electron acceptor, a Bronsted acid is a proton donor.) However, some zeolites, such as the faujasites, are unstable in acidic solutions and are activated by forming the ammonium, NH_4^+ , salt, and the heating the structure so that ammonia is driven off and the proton remains. Further heating (in both cases) will remove water from the Bronsted site, resulting in exposing a tricoordinated Al ion, which has electron-pair acceptor properties, that is, the Lewis acid site. There are wide distributions of proton donor strengths among the Bronsted acid groups in zeolites. When zeolites have low densities of proton donor groups, the proton donor strengths are high. For example, HY or HZSM-5 zeolite with a low density of acid group is like an ideal solution of dispersed non-interacting protons in a solid matrix.

Since there is one hydrogen per aluminum in the catalyst, as the amount of aluminum increases, the activity of the catalyst should also increase. The relation between aluminum content and activity for paraffin cracking and other reactions over H-Y and HZSM-5 has been noted by many authors [356-359]. The catalyst activity dependence on aluminum content does not hold when the Si/Al of most zeolites is less than 10 [356]. Activity is decreasing with a decrease in Si/Al ratio, when the Si/Al ratio is less than 10. It is argued that when the sites become too concentrated within the catalyst, they interact causing a reduction in their acidity. A maximum activity at the Si/Al ratio of about 10 for most zeolites is observed due to site – site interactions at high activities.

During the transformation of organic compounds over solid catalysts, heavy side products and/or strongly adsorbed side-products are always formed either in the pores or on the outer surface or in both positions [360], which is the most frequent cause of

catalyst deactivation in industrial processes and is of considerable technological and economical importance to the petrochemical industry [361].

In conclusion, zeolites have been widely used as support materials as well as catalysts due to their unique properties. Among them, well-defined pore structure exerts a steric influence on the reaction, controlling the access of reactants and products; high thermostability excludes the influence of zeolites on the reaction at high temperatures; remarkable acidic properties of zeolites allows researchers tune the acidity of the support as they wish to develop high efficient and environment-friendly catalysts.

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Chapter 3 Techniques of Characterization, Synthesis, and Catalytic Reactions

In the research of catalysis, various characterization techniques are indispensable to investigate the physical and chemical properties of catalysts, such as bulk and local structure, morphology, and chemical compositions, which directly effects the catalytic behaviors. Characterizing the catalysts on a molecular/atomic level before and after the reaction may reveal the catalytic process, which further illustrates the catalytic mechanism. In addition the design and modification of catalyst or the catalytic system with improved performance can be conducted more rationally and readily. Therefore understanding the fundamental concepts of the characterization techniques is absolutely necessary to appropriately take their advantage, which will be briefly described in this chapter as well as the synthesis methodologies of catalysts in this thesis.

3.1 Characterization Techniques

3.1.1 Characterization of Catalyst Morphologies and Structures

The X-Rays diffraction (XRD) technique is a useful tool to characterize the lattice space parameters of crystalline structures [1] or long range structures of other ordered materials such as mesoporous materials [1] or zeolites [2]. The chemical and structure compositions of metals or alloys can also be investigated by XRD. In addition, the average size of crystalline particles can be estimated based upon the width at half maximum of specific peaks according to the Scherrer's equation [3]. Moreover, XRD is broadly used to investigate the structure of support materials. In the cases of mesoporous molecular sieves, the XRD signals at lower angles ($1-8^\circ$) are not resulted from uniform atom arrangement in crystals leading to high angle signals ($10-80^\circ$), but

from the highly ordered pore walls [1]. 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 solution of 0.02° (2θ) in the angle range $5\text{--}80^\circ$. Prior to test, samples were dried at 373 K overnight.

Physical adsorption of nitrogen is a typical useful tool to characterize support materials. The important parameters including pore volume, specific surface area, pore size and pore size distribution could be examined from the adsorption and desorption isotherms. Normally, the BET specific surface area is acquired from the Brunauer-Emmett-Teller (BET) approach [4]. Pore volume, pore size and pore size distribution can be obtained by the Barrett-Joyner-Halenda (BJH) approach [5]. In this PhD work, nitrogen adsorption-desorption isotherms have been measured at 77 K on the Quanta Chrome static volumetric instrument Autosorb-6b station. Before tests, materials were degassed at 200°C until the residual pressure is less than 10^{-4} Torr. Baratron pressure transducer has been employed for low-pressure ($0.001\text{--}10$ Torr) measurements. Pore size and pore size distributions have been obtained via analyzing the desorption branch of isotherms.

Scanning electron microscope (SEM) is applied to directly observe the catalyst morphologies and structures. In this PhD work, the SEM image was obtained on a JEOL Field Emission Scanning Electron Microscope (JSM-6700F-FESEM). Prior to the measurements, the samples were deposited on a sample holder using an adhesive carbon tape and then decorated with gold through sputtering.

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:

$$d = \frac{\sum n_i \cdot d_i}{\sum n_i} \text{ where } \Sigma \text{ is the sum of } i \text{ over the entire sample, } n_i \text{ is the number of}$$

particles with particle diameter d_i in a certain range. The corresponding root mean square error σ was determined using the following statistical expression:

$$\sigma(d) = \sqrt{\frac{\sum n_i (d - d_i)^2}{\sum n_i - 1}}.$$

3.1.2 Characterization of Catalyst Active Sites

Wide variety of characterization techniques have been broadly adopted to study the properties of catalytic active centers like X-ray absorption near edge structure (XANES), hydrogen temperature programmed reduction (TPR), electron paramagnetic resonance (EPR), X-ray photoelectron spectroscopy (XPS) and so forth. In this study, XPS was employed to investigate the chemical state of core elements. The measurements were performed on a VG Escalab 250 spectrometer armed with Al anode (Al $K\alpha$ = 1846.6 eV), using 20 eV pass energy, 0.1 eV step and 0.15 min dwelling time. The background

chamber pressure was below 1×10^{-7} Pa. Binding energy correction was conducted concerning the C1s peak of adventitious C at 284.6 eV. Inductively Coupled Plasma (ICP) technique was applied to determine the metal contents. The samples containing metal components (both organic mixture and the solid samples), an appropriate amount of sample is taken then digested with nitric acid (69 %) at 120 °C overnight before the ICP test. The Perkin-Elmer Dual-view Optima 5300 DV ICP-OES (Optical Emission Spectrometry) system is applied in this work.

3.1.3 Characterization of Chemical Properties of Catalysts

Fourier Transform Infrared (FTIR) Spectroscopy is of the 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 CaF_2 windows. After alignment, the sample compartment was subjected to a thermal pretreatment under a helium atmosphere at 393 K for 2h to remove the moisture. The data was collected at

room temperature (resolution of 1 cm^{-1}). Diffuse Raman Supported metal oxide catalysts consist of a two-dimensional, active surface metal oxide phase that is fully dispersed and chemisorbed onto the surfaces of high surface area oxide supports (e.g. alumina, titania, silica, etc.).

Table 3.1 Infrared vibrations of chemical bonds or functional groups on CNTs surface.

Functional group	Assignment region (cm^{-1})	Reference
C-O stretch of ethers	1000-1300	[22]
Ether bridge between rings	1230-1250	
Cyclic ethers containing COCOC groups	1025-1141	
Alcohols	1049-1276, 3200-3640	
Phenolic groups:		
C-OH stretch	1000-1220	
O-H bend/stretch	1160-1200, 2500-3620	
Carbonates; carboxyl-carbonates	1100-1500, 1590-1600	
Lactones	1160-1370, 1675-1790	
Anhydrides	980-1300, 1740-1880	
Ketones ($\text{C}=\text{C}=\text{O}$)	2080-2200	
C-H stretch	2600-3000	
C-N stretch	1060-1250	[23,24]
Aromatic $\text{C}=\text{C}$ stretch	1550-1650	[24]

N-H	1650-1580	
Amines oscillation and stretch	1640 and 1728	[25]
CNTs backbone	1554	
Conjugated C=O stretch	1677	[35]
Amide C=O	1650	
S-H	2200	
COOH	1025, 1182, 1727, 3428	[26]
C=N	1570, 1639	

Vibrational spectroscopy such as Raman has often been used to probe the molecular structures of supported metal oxides; a large amount of information has been obtained for the supported metal oxide catalysts. Ultraviolet Raman spectroscopy has been proved to be a powerful technique for the study of catalysts and other solids, especially for the identification of isolated transition metal atoms substituted in the framework of molecular sieves. In this thesis, the supported zeolite catalysts were studied by Raman spectroscopy in order to identify the structure of the metal incorporated into the silica framework. Raman spectra were collected on a Renishawin Via Raman system with a 325 nm laser as the excitation source. A laser output of 30 mW was employed and the maximum incident power at the sample was approximately 6 mW.

To verify the successful doping of nitrogen atoms into the carbon nanotube system, elemental analyses (EA), as a powerful technique, is applied to determine the chemical composition of pristine and nitrogen-doped carbon nanotubes. Different from X-ray photoelectron spectroscopy (XPS), which can determine the chemical states of various

elements, EA can give the total content of specific element such as carbon, nitrogen, sulfur, and hydrogen by heating the sample in high temperatures and analyzing the as-result gaseous mixture. If other elements are absent, the oxygen content can even be obtained by a simple subtraction method. In this dissertation, EA were obtained from a EuroVector Euro EA elemental analyzer.

3.2 Synthesis Methodologies

3.2.1 Materials

Titanium dioxide nanopowders (P25, Aeroxide), Sodium Chloride (NaCl, 99.0%, Fisher Scientific), Sodium Phosphate Dibasic Heptahydrate ($\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$, 99.3%, Fisher Scientific), PdCl_2 (>99%, Aldrich), Titanium dioxide nanopowders (P90, Aeroxide), Chloric Acid (HCl, 36-38 wt.%), sodium hydroxide (NaOH, >98%, Sigma-Aldrich), CNT (>95%, Cnano), Hydrazine Monohydrate ($\text{H}_4\text{N}_2 \cdot \text{H}_2\text{O}$, >98.0%, Tokyo Chemical Industry Co., LTD.), Gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 99\%$, Sigma-Aldrich), Silver nitrate (AgNO_3 , $\geq 99\%$, Sigma-Aldrich), Chloroplatinic acid hydrate ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, ~38% Pt basis Aldrich), Ruthenium(III) chloride hydrate ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, 38.0-42.0% Ru basis, Aldrich), Ammonium hydroxide solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28.0-30.0%, Sigma-Aldrich), Dicyandiamide (99%, Aldrich), Hydroxylamine Chloride (99%, Sigma-Aldrich), Hexamethylenetetramine (HMT, $\geq 99.0\%$, Sigma-Aldrich), Urea (99%, Sinopharm), Cobalt (II) Chloride anhydrous (97%, Alfa Aesar), Sulphuric acid (95 wt.%, VWR International), Titanium (IV) n-butoxide ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$, >99%, Alfa Aesar), Acetic acid (glacial, 100%, Merck), Ethanol (>99.5%, Sigma-Aldrich), Benzene (>99.9%, Sigma-Aldrich) and Toluene (>99.9%, Sigma-Aldrich), Tetraethyl orthosilicate (TEOS, 98%, Sinopharm) and, Ethyl acetate

(EA, >99.5%, Sigma- Aldrich), (3-aminopropyl) triethoxysilane (APS, $\geq 98\%$, Sigma-Aldrich), benzyl alcohol anhydrous (>99.8%, Sigma-Aldrich), benzaldehyde (>99.5%, Aldrich), benzoic acid (>99.5%, Sigma-Aldrich), toluene anhydrous (>99.8%, Sigma-Aldrich), ethanol (>99.5%, Sigma-Aldrich), Acetone (CH_3COCH_3 , HPLC grade, Fisher Scientific).

3.2.2 Preparation of Titanium Dioxide Nanowires

TiO_2 nanowires were synthesized by using a molten salt flux method according to Dr. Liu's report [22]. In a typical synthesis, 2 g of P25 nanopowders, 8 g of NaCl, and 3.0192 g of $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ were ground with mortar and pestle to form a fine mixture. Then the mixture was transferred to a crucible and calcined inside a box furnace at 1098 K for 8 hours. After calcination, the crucible was cooled to room temperature, and the calcined mixture was washed in boiling deionized water extensively to remove all soluble salts. Transition metal doped TiO_2 nanowires were prepared by adding a certain amount of transition metal precursors.

3.2.3 Preparation of Palladium Catalysts Supported On Titanium Dioxide Nanomaterials

Palladium catalysts supported on titanium dioxide nanomaterials are prepared by two methods: deposition-precipitation with urea (DP) and wet impregnation method (IMP).

In a typical experiment for the DP method, 1.0 g of TiO_2 was dispersed in 50 mL of 1.0 M urea solution under vigorous stirring. To prepare yield 0.5 wt.%, 1.0 wt.%, and 2.0 wt.% monometallic catalysts, 1.0 ml, 2.0 ml, 4.0 ml of 0.05 M PdCl_2 aqueous solution were added to the above suspension respectively. The temperature of the

suspension was slowly increased to 80 °C and maintained at this temperature for 6 hours to allow the decomposition of urea. After cooling down to room temperature, the suspension was thoroughly washed with ultra-pure water and dried at 80 °C oven overnight. The solids were then ground with a mortar and pestle and then calcined at 400 °C in air for 3 hours. The catalysts are activated in a H₂ flow of 20 ml/min at 400 °C for 2 h and are employed for subsequent characterization and activity test.

In a typical experiment for the IMP method, 1.0 ml, 2.0 ml, 4.0 ml of 0.05 M PdCl₂ aqueous solution were added to 1.0 g of TiO₂ to yield 0.5 wt.%, 1.0 wt.%, and 2.0 wt.% monometallic catalysts, respectively. Appropriate amount of ultra-pure water was added to the above suspension to maintain the total volume of liquid injected 4 mL. The paste formed was allowed to vaporize slowly at 80 °C with vigorously stirring. The solids obtained were further dried at 80 °C oven and then were well ground with mortar and pestle and then calcined in static air, typically 400 °C for 3 h. The catalysts activated in a H₂ flow of 20 ml/min at 400 °C for 2 h are used for characterization and activity test.

3.2.4 Purification and Preparation of CNTs Functionalized With Oxygen-Containing Groups

Commercial multi walled CNTs powder (>95%, Cnano) was purified with pretreatment in concentrated nitric acid and oxygen-containing groups were generated on CNT surfaces: slurry of CNTs powder (2 g) suspended into concentrated nitric acid (69%, Sigma-Aldrich) was refluxed at 120 °C for 4h. After cooling to room temperature, vacuum filtration was performed followed by rinse with deionized water for four times and subsequently drying at 80 °C overnight.

This step was frequently employed to make CNTs pre-treated with concentrated nitric acid in order to remove the metallic impurities as well as the amorphous carbon following the processes described by Lordi et al.

3.2.5 Preparation of Nitrogen-Doped Carbon Nanotubes

N-CNTs with different nitrogen sources were prepared according to nitrogen-doped graphene synthesis procedures [23-31].

Typically, for the methods using hydrazine hydrate as nitrogen source, the detailed procedure is as follows: 300 mg CNT were added to 20 mL ultra-pure water. The pH of the solution was adjusted to 10 using diluted ammonia solution. Subsequently, 5 mL of hydrazine hydrate was added with vigorously stirring for 30 minutes. The solution was transferred into a 50 mL Teflon-lined autoclave with a total volume of 35 mL and heated at 180 °C for 12 hours. The products were washed thoroughly with ultra-pure water and ethanol several times and the solid obtained were dried under vacuum at 40 °C for 12 hours. The support materials was denoted as CNT-N-1.

For the methods using urea as nitrogen source, the detailed procedure is as follows: 300 mg CNT were dispersed into 25 mL ultra-pure water. Then 3 g urea was added into the dispersion under vigorously stirring for at least 30 minutes. After that, the solution was transferred into a 50 mL Teflon-lined autoclave with a total volume of 35 mL and heated at 180 °C for 12 hours. The products were washed thoroughly with ultra-pure water and ethanol several times and the solid obtained were dried under vacuum at 40 °C for 12 hours. The support materials was denoted as CNT-N-2.

For the methods using Hexamethylenetetramine (HMT) as nitrogen source, the detailed procedure is as follows: 300 mg CNT were dispersed into 25 mL ultra-pure

water. Then 3 g HMT was added into the dispersion under vigorously stirring for at least 30 minutes. After that, the solution was transferred into a 50 mL Teflon-lined autoclave with a total volume of 35 mL and heated at 180 °C for 12 hours. The products were washed thoroughly with ultra-pure water and ethanol several times and the solid obtained were dried under vacuum at 40 °C for 12 hours. The support materials was denoted as CNT-N-3.

For the methods using Dicyandiamide as nitrogen source, the detailed procedure is as follows: 300 mg CNT and 1.5 g Dicyandiamide were added into 30 mL ultra-pure water. The mixture was put into an ultrasonic bath to facilitate the dissolution of Dicyandiamide. After that, the solution was transferred into a 50 mL Teflon-lined autoclave with a total volume of 35 mL and heated at 180 °C for 12 hours. The products were washed thoroughly with ultra-pure water and ethanol several times and the solid obtained were dried under vacuum at 40 °C for 12 hours. The support materials was denoted as CNT-N-4.

For the methods using Hydroxylamine Chloride (HACl) as nitrogen source, the detailed procedure is as follows: 300 mg CNT and 2.1 g HACl were added into 30 mL ultra-pure water. The mixture was put into an ultrasonic bath to facilitate the dissolution of Dicyandiamide. After that, the solution was transferred into a 50 mL Teflon-lined autoclave with a total volume of 35 mL and heated at 180 °C for 12 hours. The products were washed thoroughly with ultra-pure water and ethanol several times and the solid obtained were dried under vacuum at 40 °C for 12 hours. The support materials was denoted as CNT-N-5. For nitrogen-doped carbon nanotubes with different amount of hydroxylamine chloride as nitrogen source, the as-prepared carbon nanotubes are

denoted as CNT-HACl-1, CNT-HACl-2, CNT-HACl-3, CNT-HACl-4, CNT-HACl-5, CNT-HACl-6.

3.2.6 Preparation of Palladium Catalysts Supported on Carbon Nanotubes and Nitrogen-Doped Carbon Nanotubes

Palladium catalysts supported on carbon nanotubes and nitrogen-doped carbon nanotubes are prepared by two methods: deposition-precipitation with urea (DP) and ionic absorption-reduction method (AR) [33].

In a typical experiment for the DP method, 1.0 g of supporting material was dispersed in 50 mL of 1.0 M urea solution under vigorous stirring. To prepare yield 2.0 wt.% monometallic catalysts, 4.0 ml of 0.05 M PdCl₂ aqueous solution were added to the above suspension respectively. The temperature of the suspension was slowly increased to 80 °C and maintained at this temperature for 6 hours to allow the decomposition of urea. After cooling down to room temperature, the suspension was thoroughly washed with ultra-pure water and dried at 80 °C oven overnight. The catalysts are activated in a H₂ flow of 20 ml/min at 400 °C for 2 h and are employed for subsequent characterization and activity test.

In a typical experiment for the AR method, 1.0 g of supporting material was dispersed in 50 mL of ultra-pure water under vigorous stirring. To prepare yield 2.0 wt.% monometallic catalysts, 4.0 ml of 0.05 M PdCl₂ aqueous solution were added to the above suspension respectively. The temperature of the suspension was slowly increased to 80 °C and maintained at this temperature for 6 hours. After cooling down to room temperature, the suspension was thoroughly washed with ultra-pure water and dried at

80 °C oven overnight. The catalysts are activated in a H₂ flow of 20 ml/min at 400 °C for 2 h and are employed for subsequent characterization and activity test.

3.2.7 Preparation of Palladium Catalysts Supported on Zeolites

Noble nanoparticle catalysts supported on zeolites were prepared by a deposition-precipitation method. An appropriate amount of noble metal salt (PdCl₂, HAuCl₄, H₂PtCl₆, or AgNO₃) was dissolved into water, the aqueous solution was added to 0.5 g zeolite, ZSM5, HY, HB or MOR, followed by adding sufficient amount of urea suspended in 30 mL deionized water, followed by vigorous stirring at 80 °C for 6 h. The catalyst were obtained by filtering and washing with deionized water, and dried at 60 °C overnight. The catalysts were calcined at 300 °C for 4 h in air and then reduced at 400 °C for 2 h with hydrogen flow of 20 mL/min. All catalysts were donated as 1Pd/HY (1 % Pd for weight percent), 2Pd/HY (2 % Pd for weight percent), the others were like them, number means weight percent, listed in table 2. 2PdO/HY means the sample was prepared without the last procedure, reduction by hydrogen.

3.3 Catalytic Reactions

3.3.1 Benzyl Alcohol Oxidation Using Palladium Catalysts Supported On Titanium Dioxide Nanomaterials

The catalytic reaction of benzyl alcohol using palladium nanoparticles supported on titanium dioxide nanomaterials were and pure oxygen as oxidant were conducted under atmospheric pressure. As effects of reaction temperature, catalysts/substrate weight ratio, reaction duration and oxygen flow rate are all studied, reaction parameters can be modified according to specific condition. Therefore, one typical reaction condition can be expressed as below: 5.174 mL of benzyl alcohol was added into a 25 mL three-

necked glass flask pre-charged with 20 mg of catalysts. The flask was immersed in a silicone oil bath and then slowly heated to 160 °C. Pure oxygen with a flow rate of 20 mL min⁻¹ is bubbled to initiate the reaction. The reaction ran for 1 h under vigorous stirring at the speed of 1200 rpm. After the reaction, the solid catalyst was filtrated and the liquid phase was analyzed by an Agilent gas chromatography 6890 armed with HP-5 capillary column. Dodecane was the internal standard to quantify the percentage of residual reactant and products in order to evaluate benzyl alcohol conversion and benzaldehyde selectivity [42]. The definition of conversion, selectivity:

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

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

3.3.2 Benzyl Alcohol Oxidation Using Palladium Catalysts Supported On Carbon Nanotubes and Nitrogen-Doped Carbon Nanotubes Nanomaterials

The catalytic reaction of benzyl alcohol using palladium nanoparticles supported on titanium dioxide nanomaterials were and pure oxygen as oxidant were conducted under atmospheric pressure. In a typical reaction, 5.174 mL of benzyl alcohol was added into a 25 mL three-necked glass flask pre-charged with 20 mg of catalysts. The flask was immersed in a silicone oil bath and then slowly heated to 160 °C. Pure oxygen with a flow rate of 20 mL min⁻¹ is bubbled to initiate the reaction. The reaction ran for 3 hours under vigorous stirring at the speed of 1200 rpm. After the reaction, the solid catalyst was filtrated and the liquid phase was analyzed by an Agilent gas chromatography 6890 armed with HP-5 capillary column. Dodecane was the internal standard to quantify the

percentage of residual reactant and products in order to evaluate benzyl alcohol conversion and benzaldehyde selectivity [34].

3.3.3 Ethyl Alcohol Oxidation Using Palladium Catalysts Supported Zeolites

The ethylene partial oxidation was carried out in a fixed-bed reactor under atmospheric pressure. 100 mg powder catalyst was loaded for each run. The feed was a mixture of ethanol and O₂ (2:1 mol) in He with the flow of 0.016 ml/min ethanol, 3ml/min O₂ and 22.4 ml/min He. The temperature was increased from 60 °C to 300 °C and was maintained for 30 min at each set temperatures for measurement, i.e. 60, 80, 90, 120, 150, 180, 210, 250, and 300 °C. For each step the increase of the temperature took 30 min. The outlet gas was analyzed on-line by an Agilent gas chromatograph 7890 equipped with a 3 m packed Q column and a TCD detector as well as another Agilent gas chromatograph 7890 with a DB-WAX capillary column (60 m) and flame ionization detector (FID).

List of Abbreviations

CNTs	Multi-Walled Carbon Nanotubes
EA	Ethyl Acetate
EtOH	Ethanol
FID	Flame Ionization Detector
FTIR	Fourier Transform Infrared Spectroscopy
GC-MS	Chromatography-Mass Spectrometry
ICP	Inductively Coupled Plasma
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscopy
UV	Ultraviolet
UV-vis	UV-visible
XPS	X-ray Photoelectron Spectroscopy
XRD	X-Rays Diffraction
DP	Deposition-Precipitation With Urea Method
IMP	Wet Impregnation Method
AR	Absorption-Reduction Method
HMT	Hexamethylenetetramine
HACl	Hydroxylamine Chloride

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Chapter 4 Palladium Nanoparticles supported on TiO₂ nanomaterials for Benzyl Alcohol Oxidation

Selective oxidation of benzyl alcohol into its corresponding carboxyl compounds have been an important issue in chemical engineering as the obtained products are essential raw materials for the synthesis of other fine chemicals, spanning from pharmaceutical, dyestuff, agrochemical and perfume industries. Another reason is its simplicity as a model reaction to investigate the mechanism involved and to test the activity of catalysts. Initially, inorganic compounds such as ruthenium oxides [1, 2], chromium reagents [3-6], and permanganates [7, 8] are employed as oxidants due to their high oxidative ability as well as moderate selectivity. However, its drawbacks are also apparent: harmful reagents, low products yields, metal wastes and time-consuming separation and purification steps [4]. Therefore, looking for inexpensive, environmentally benign oxidants has becoming more and more important. Recently, inexpensive and environmentally friendly oxidants including hydrogen peroxide, air or pure oxygen have shown its ability to replace these conventional ones, with water the sole byproduct in these reaction [9, 10]. More importantly, by designing appropriate catalysts, both high activity and high selectivity can also be achieved at the same time.

Noble metal-based catalysts, especially those in the platinum group such as ruthenium [11, 12], and other noble-metal catalysts like gold [13-15], have widely been used in alcohol oxidations due to their superior activity and mature experimental synthesis procedures. Compared to other members of this group, palladium is particularly attractive [15-20]. Palladium catalysts supported on different materials including transition metal oxides, carbon nanotubes, hydroxyapatite, and many others

have been extensively studied in benzyl alcohol oxidation. Apart from the effects of supporting materials, the particle size is also of vital importance. More recently, a molten salt reflux method has been developed to prepare high-quality, single-crystalline titanium dioxide nanowires with controllable dimensions [21]. Compared to conventional hydrothermal or templates methods, it's much more time-saving and can be produced in large scale, which is a big advantage.

Therefore, in this chapter, the effects of different supporting materials will be investigated by depositing palladium catalysts on commercially available titanium dioxide nanoparticles P25 and titanium dioxide nanowires prepared by molten salt reflux method. Two different methods, namely, incipient wetness impregnation method (IMP) and urea-assisted deposition-precipitation method (DP) will be employed to synthesize catalysts with different sizes and distributions, and their catalytic performance will be studied by the selective oxidation of benzyl alcohol.

4.1 Pd@P25-IMP Catalysts for Benzyl Alcohol Oxidation

4.1.1 Characterization of Pd@P25-IMP catalysts

The XRD patterns of P25 nanoparticles as well as standard rutile and anatase are shown in Figure 4.1.1. The diffraction peaks at 2θ of 25.2° , 37.8° , 48.0° , 53.9° , 55.1° , 62.7° , 68.8° , 70.3° , 75.0° are attributed to the (101), (004), (200), (105), (211), (204), (116), (220), (215) facets of anatase titanium dioxide; the diffraction peaks at 2θ of 27.5° , 36.1° are attributed to the (110) and (101) facets of rutile titanium dioxide. The relative intensities of these two phases further confirm the composition of P25 is an anatase-rich nanomaterial.

Figure 4.1.1 XRD patterns of P25, standard rutile (green line) and standard anatase (red line) titanium dioxide.

Figure 4.1.2 shows the XRD patterns of a series of palladium catalysts supported on P25 prepared by an incipient wetness impregnation method as well as that of P25. It can be clearly seen apart from the intense peaks attributed to P25 nanostructure, no discernable peaks of palladium are observed even for 2.0 wt.% palladium catalysts, suggesting that the palladium nanostructures are highly dispersed on the titanium

dioxide nanostructures. The dispersion of nanostructures was further investigated by TEM, and the results are illustrated in Figure 4.1.3.

Figure 4.1.2 XRD patterns of P25, 0.5Pd@P25-IMP, 1.0Pd@P25-IMP, and 2.0Pd@P25-IMP catalysts.

Figure 4.1.3 TEM images of 2.0Pd@P25-IMP catalysts.

Figure 4.1.3 shows the TEM images of 2.0Pd@P25-IMP catalysts. It can be seen from the image that P25 are titanium dioxide nanoparticles with a primary particle size of 30-50 nanometers while based on 50 particles' counting, 2.0Pd@P25-IMP catalysts show a mean particle size at around 8 nm with a relative narrow size distribution, suggesting the successful loading of palladium catalysts on P25 nanomaterials. It should be mentioned that due to the low loadings of palladium on 0.5Pd@P25-IMP, 1.0Pd@P25-IMP catalysts, it is very difficult to obtain TEM pictures of them, which can be further confirmed by the palladium loadings for each catalyst obtained by ICP.

Table 4.1.1 Palladium contents on Pd@P25-IMP catalysts prepared by wetness impregnation method.

Catalysts	Pd ^a (wt.%)	Pd ^b (wt.%)
0.5Pd@P25-IMP	0.5	0.45
1.0Pd@P25-IMP	1.0	0.92
2.0Pd@P25-IMP	2.0	1.89

^a Theoretical metal content.

^b Metal content was obtained by ICP.

^a Theoretical metal content.

^b Metal content was obtained by ICP.

Table 4.1.1 shows the palladium loadings for these three catalysts. Under acidic conditions, negatively charged Pd complexes in HCl containing solution are readily attracted to the positively charged P25 surfaces. Therefore, with the evaporation of the

solvent at 80 °C, almost 90% of the palladium precursor in the solution can be deposited on the titanium nanostructures, implying the applicability of wet impregnation as a powerful technique to prepare palladium catalysts supported on titanium dioxide materials.

4.1.2 Temperature Effects

Temperature can play a vital role in chemical reactions. Chen et al has investigated the temperature effect of palladium catalysts supported on mesoporous silica and found that when the temperature was increased from 100 °C to 160 °C, a tenfold enhancement in benzyl alcohol conversion was observed [22]. Therefore, the temperature effects of palladium catalysts using titanium dioxide as supports were also investigated in this dissertation.

Table 4.1.2 shows the catalytic results of benzyl alcohol oxidation over Pd@P25-IMP catalysts conducted at different temperatures. It should be mentioned that the support material has almost no activity towards substrate conversion and therefore the reaction is only attributed to the presence of palladium catalysts. In the temperature range from 80 to 160 °C, benzaldehyde is the major product, with toluene the only byproduct for all the three catalysts. For each catalyst, the conversion of benzyl alcohol is extremely low at low temperatures, while a more than fivefold enhancement was obtained when the reaction system was increased to 100 °C, and reaches the maximum at 120 °C, with almost a half of the reactants converted. It is quite interesting when the temperature is further increased, the conversion reacts in an opposite way. In Chen's report, the palladium catalysts reach its best reactivity when the temperature was set 160 °C.

Increasing temperature might not be favorable for better conversion, but, it is capable of increasing the selectivity of benzaldehyde. At low temperatures, quite a small amount of the reactants are reacting with the catalysts with high selectivity towards aldehyde. When the temperature is elevated to 100 °C, more substrates are converted at the expense of aldehyde selectivity and reaches its maximum at 120 °C with the lowest selectivity. However, when the temperature is further increased, the selectivity increases gradually with the decrease of conversion. It is believed the disproportionation reaction is the source of toluene production during benzyl alcohol transformation [23], which can be represented by reaction (a). At the same time, the selective oxidation of benzyl alcohol into benzaldehyde using oxygen as oxidant is undergoing. Therefore, the overall reaction is the combination of these two seemingly independent paths.

Table 4.1.2 Catalytic results of benzyl alcohol oxidation over Pd@P25-IMP catalysts at different temperatures.

Catalysts	Temperat °C	Conversion (%)	Selectivity (%)	
			Benzaldehyde	Toluene
0.5Pd@P25-IMP	80	4.1	60.6	39.4
0.5Pd@P25-IMP	100	22.3	50.0	50.0
0.5Pd@P25-IMP	120	45.9	61.6	38.4
0.5Pd@P25-IMP	140	33.3	65.5	34.5
0.5Pd@P25-IMP	160	20.4	83.4	16.6
1.0Pd@P25-IMP	80	1.6	81.6	18.4
1.0Pd@P25-IMP	100	11.4	69.4	30.6
1.0Pd@P25-IMP	120	52.9	62.4	37.6

1.0Pd@P25-IMP	140	26.2	68.0	32.0
1.0Pd@P25-IMP	160	17.3	78.1	21.9
2.0Pd@P25-IMP	80	0.77	100.0	0.0
2.0Pd@P25-IMP	100	11.3	62.4	37.6
2.0Pd@P25-IMP	120	52.0	61.9	38.1
2.0Pd@P25-IMP	140	27.5	74.8	25.2
2.0Pd@P25-IMP	160	23.2	78.7	21.3

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

¹; reaction time, 1h.

In heterogeneous catalysis, reactions involve the adsorption of substrates on the active sites of the catalysts, subsequent activation and reaction, and finally, desorption of the products from the catalysts [24]. Sometimes products especially the byproducts are reluctant to leave the active sites of the catalysts and thus resulting in deactivation of the catalysts. In present catalytic system, most of the components can be classified into four compounds: the reactant – benzyl alcohol, the desired product – benzaldehyde, two byproducts – toluene and water. Therefore, the influence of each component can be investigated by a screening method. Taking the composition of 2.0 Pd@P25-IMP catalytic system after 1 hour reaction as an example, 52% conversion of benzyl alcohol indicates there are 9.28 mmol toluene, 9.28 mmol water, 16.12 mmol benzaldehyde and 24 mmol benzyl alcohol left in the system.

Table 4.1.3 Catalytic results of benzyl alcohol oxidation over 2.0Pd@P25-IMP

catalysts when various products are present in the reaction system.

Catalysts	Toluene mmol	Benzaldehyde mmol	Water mmol	Conversion	Selectivity (%)	
				(%)	Benzaldehyde	Toluene
2.0Pd@P25-IMP	9.28	16.12	9.28	51.4	65.3	34.7

2.0Pd@P25-IMP	9.28	0	9.28	20.2	50.0	50.0
2.0Pd@P25-IMP	9.28	16.12	0	60.7	66.5	33.5
2.0Pd@P25-IMP	0	16.12	9.28	40.3	92.5	7.5

^a Reaction conditions: catalyst, 20 mg; temperature, 120 °C; benzyl alcohol, 24 mmol; O₂, 20 mL min⁻¹; reaction time, 1h.

Table 4.1.3 shows the catalytic results of benzyl alcohol oxidation over 2.0Pd@P25-IMP catalysts when various products are present in the reaction system. It can be seen that in the presence of toluene, water and benzaldehyde, the fresh catalysts can transform benzyl alcohol with same conversion and same aldehyde selectivity as those without any of these products. However, when one and only one of these three products is removed, the catalysts have quite different behaviors, verifying the actual composition of the system after 1 hour reaction in a reverse way. When benzaldehyde is removed from the system initially, much less benzyl alcohol participated in the reaction and are exclusively transformed in the disproportion route, with 50% selectivity towards toluene and the other 50% towards aldehyde, suggesting removal of desired products results in the poisoning of catalysts by the two byproducts. Separating toluene from the reaction system have similar effects in benzyl alcohol conversion. However, when only water is removed, the catalysts show higher activity and slightly better aldehyde selectivity, suggesting water is the main reason for catalysts deactivation. It should be mentioned that in the absence of toluene, much higher selectivity towards benzaldehyde is observed, indicating the presence of toluene might “induce” the continuous production of toluene through the disproportion reaction. As discussed earlier, only the disproportion path is activated at the very beginning, resulting in equimolar toluene and benzaldehyde. Therefore, removal of the toluene produced at

early stages in time might be able to limit the reaction to be conducted only in route (b), resulting in almost 100% selectivity towards aldehyde.

4.1.3 Reaction Duration Effects

Reaction duration test is a powerful technique to examine the ability of catalysts to continuously catalyze the substrate transformation. Table 4.1.4 shows the catalytic results of benzyl alcohol oxidation over Pd@P25-IMP catalysts for different reaction durations at 120 °C, the optimum temperature for Pd@P25-IMP catalysts. It can be seen, as the reaction proceeds, the selectivity towards aldehydes are increasing for all of the three catalysts, implying the oxidative path precedes the disproportionation one. More importantly, almost 40% of the converted benzyl alcohol transformed into toluene in the first 0.5 hour, accompanying which 40% of the converted alcohol are catalyzed into benzaldehyde. Therefore, it is reasonable to predict that initially only the disproportionation reaction occurs and as time proceeds, the oxidation reaction is triggered, and gradually match the disproportionation path about 2 hours later, and finally exceeds the former one, resulting the much high aldehyde selectivity in the end.

Table 4.1.4 Catalytic results of benzyl alcohol oxidation over Pd@P25-IMP catalysts for different reaction durations.

Catalysts	Reaction Time (h)	Conversion (%)	Selectivity (%)	
			Benzaldehyde	Toluene
0.5Pd@P25-IMP	0.5	24.1	56.4	43.6
0.5Pd@P25-IMP	1.0	45.9	61.6	38.4
0.5Pd@P25-IMP	2.0	61.1	69.3	30.7
0.5Pd@P25-IMP	4.0	80.5	74.3	25.7
1.0Pd@P25-IMP	0.5	34.5	60.0	40.0

1.0Pd@P25-IMP	1.0	52.9	62.4	37.6
1.0Pd@P25-IMP	2.0	58.8	68.0	32.0
1.0Pd@P25-IMP	4.0	67.4	77.8	22.2
2.0Pd@P25-IMP	0.5	25.2	61.5	38.5
2.0Pd@P25-IMP	1.0	52.0	61.9	38.1
2.0Pd@P25-IMP	2.0	47.4	73.4	26.6
2.0Pd@P25-IMP	4.0	46.9	82.0	18.0

^a Reaction conditions: catalyst, 20 mg; benzyl alcohol, 50 mmol; O₂, 20 mL min⁻¹; temperature, 120 °C.

4.1.4 Catalyst/Substrate Weight Ratio Effects

Apart from the temperature and reaction duration effects, other parameters are also investigated. Table 4.1.5 shows the catalytic results of benzyl alcohol oxidation over Pd@P25-IMP catalysts at different catalysts/substrate ratios. Keeping the amount of benzyl alcohol constant, different amounts of catalysts are charged into the catalytic system. As seen from the table and figure, when 5 mg of catalysts are used, the substrate can be transformed in the highest selectivity towards aldehyde with quite low conversion. With the increase of catalysts, the aldehyde selectivity gradually decrease, from 93.1% to 60.4% for 1.0 Pd@P25-IMP, which is quite dramatic. As discussed earlier, initially, only the disproportionation path occur and for some reason the oxidative path is triggered later. Accompanied by the former path are equimolar amounts of benzaldehyde and toluene and only aldehyde is produced in the latter route. Therefore, the accumulation of toluene will be much more profound with more catalysts added into the system, resulting poorer aldehyde selectivity in the end. Continuing taking 1.0 Pd@P25-IMP as an example, about 67% of the obtained aldehyde can be attributed to the disproportionation reaction of alcohol in the first 30 min, while the

number is 60% when time duration is prolonged to 1 hour, still more than 50%. As for conversion, mass transfer problems may occur due to the insufficient agitation of the mixture, thus resulting lower conversion when 40 mg catalysts are charged into the system [25].

Table 4.1.5 Catalytic results of benzyl alcohol oxidation over Pd@P25-IMP catalysts at different catalysts/substrate ratios.

Catalysts	Weight of Catalysts (mg)	Conversion (%)	Selectivity (%)	
			Benzaldehyde	Toluene
0.5Pd@P25-IMP	5	13.4	72.9	27.1
0.5Pd@P25-IMP	10	30.3	66.1	33.9
0.5Pd@P25-IMP	20	45.9	61.6	38.4
0.5Pd@P25-IMP	40	41.5	62.2	37.8
1.0Pd@P25-IMP	5	6.1	93.1	6.9
1.0Pd@P25-IMP	10	24.3	67.3	32.7
1.0Pd@P25-IMP	20	52.9	62.4	37.6
1.0Pd@P25-IMP	40	41.1	60.4	39.6
2.0Pd@P25-IMP	5	10.6	81.0	19.0
2.0Pd@P25-IMP	10	41.3	64.6	15.4
2.0Pd@P25-IMP	20	52.0	61.9	38.1
2.0Pd@P25-IMP	40	21.7	70.8	29.2

^a Reaction conditions: benzyl alcohol, 50 mmol; O₂, 20 mL min⁻¹; time, 1h; temperature, 120 °C.

4.1.5 Oxygen Flow Rate Effects

In Chen's report, when the oxygen flow rate was further increased from 20 mL min⁻¹, deeper oxidative reactions like from benzaldehyde into benzoic acid can occur. Therefore, oxygen flow rate is another important factor to obtain aldehyde in high yields

with high selectivity. Table 4.1.6 shows the catalytic results of benzyl alcohol oxidation over Pd@P25-IMP catalysts at different oxygen flow rates. Quite interestingly, with the increase of oxygen flow rate from 5 mL min⁻¹ to 40 mL min⁻¹, no deeper oxidative products like benzoic acid or other byproducts are obtained, suggesting the excellent controllability of these catalytic systems in inhibiting deep oxidative reactions. Although oxygen is not directly participate in the disproportionation reaction, it's difficult to determine the amount of amount of aldehyde produced from the oxidative path due to the promotional effect of oxygen to the disproportionation route [23]. Therefore, only an overall influence of oxygen flow rate on the benzyl alcohol oxidation can be obtained.

Another surprising point is the conversion. When the oxygen flow rate was increased from 5 to 20 mL min⁻¹, more oxygen are available to participate in the oxidative reaction, resulting in more alcohol being converted. However, when 40 mL min⁻¹ of oxygen was bubbled into the system, the conversion is becoming lower. It should be mentioned that the well mixed system of oxygen, catalysts and substrate is essential to the oxidative path. When high flow rate of oxygen was injected through a syringe needle, the mixture of catalysts and substrate may be blown away even before the oxygen participate in the reaction, thus resulting in less conversion.

Table 4.1.6 Catalytic results of benzyl alcohol oxidation over Pd@P25-IMP catalysts at different oxygen flow rates.

Catalysts	Oxygen Flow Rate (mL min ⁻¹)	Conversion (%)	Selectivity (%)	
			Benzaldehyde	Toluene
0.5Pd@P25-IMP	5	29.6	57.9	42.1

0.5Pd@P25-IMP	10	34.1	62.4	37.6
0.5Pd@P25-IMP	20	45.9	61.6	38.4
0.5Pd@P25-IMP	40	22.0	68.0	32.0
1.0Pd@P25-IMP	5	33.2	57.6	42.4
1.0Pd@P25-IMP	10	50.5	60.4	39.6
1.0Pd@P25-IMP	20	52.9	62.4	37.6
1.0Pd@P25-IMP	40	54.2	61.4	38.6
2.0Pd@P25-IMP	5	32.2	63.3	36.7
2.0Pd@P25-IMP	10	35.8	63.6	36.4
2.0Pd@P25-IMP	20	52.0	61.9	38.1
2.0Pd@P25-IMP	40	31.1	66.8	33.2

^a Reaction conditions: catalyst, 20 mg; benzyl alcohol, 50 mmol; time, 1h; temperature, 120 °C.

4.2 Pd@P25-DP Catalysts for Benzyl Alcohol Oxidation

4.2.1 Characterization of Pd@P25-DP catalysts

Figure 4.2.1 shows the XRD patterns of a series of palladium catalysts supported on P25 prepared by a deposition-precipitation method as well as that of P25. Similar to the XRD patterns of Pd@P25-IMP catalysts, apart from the intense peaks attributed to P25 nanostructure, no discernable peaks of palladium are observed even for 2.0 wt.% palladium catalysts, suggesting that the palladium nanostructures are highly dispersed on the titanium dioxide nanostructures. The dispersion of nanostructures was further investigated by TEM, and the results are illustrated Figure 4.2.2.

Figure 4.2.1 XRD patterns of P25, 0.5Pd@P25-DP, 1.0Pd@P25-DP, and 2.0Pd@P25-DP catalysts.

Figure 4.2.2 TEM images of 2.0Pd@P25-DP catalysts.

Compared to sodium dioxide, urea can gently adjust the pH of the solution containing transition metal ions by releasing ammonia at elevated temperature, thus resulting in smaller metal particles with narrower size distribution [26]. Therefore, it has been widely used to precipitate transition metal catalysts on metal oxide supports [27]. Kittisakmontree has investigated the influence of deposition-precipitation method on the as-prepared palladium catalysts prepared by incipient wetness impregnation method [28]. It is found that with the addition of gold solution by deposition-precipitation method, the mean palladium particle size can decrease from 6.9 nm to 2.0 nm with a narrower distribution. The redispersion and restructuring process of palladium nanoparticles can occur even in the absence of gold ions under the same condition, proving that deposition-precipitation method is capable of decreasing the particle size as well as increasing the dispersion of palladium catalysts on titanium dioxide support. It can be seen from Figure 4.2.2 that the mean particle size of palladium catalysts are below 2 nm with a narrower size distribution. However, compared to that of 2.0Pd@P25-IMP catalysts, very few nanoparticles are observed, implying the small loadings of palladium ions on the surface of titanium dioxide.

Table 4.2.1 shows the palladium loadings of a series of palladium catalysts prepared by a deposition-precipitation method. Even with the increase of precursor concentration from 0.001 mol L⁻¹ to 0.004 mol L⁻¹, the total loadings of palladium have almost no change, which is quite confusing compared to gold catalysts prepared in the same way. As we all know, at temperatures above about 330K following reactions can occur [26].

For transition metal ions like gold, precipitates are formed and deposited quickly at very low pH, followed by a slow deaggregation step when the pH of the solution increases with the decomposition of urea [29]. For palladium, however, it's not the case. Due to large amounts of hydroxyl groups attached to the surface of titanium dioxide nanoparticles, P25 has a isoelectric point close to 6.2 [30], resulting in negative zeta potential when urea decomposes. At the same time, platinum group elements like platinum itself and palladium ions can combine the chlorine anions and ammonia to form coordination complexes, such as $[\text{PdCl}_4]^{2-}$ or $[\text{PdCl}_3\text{NH}_3]^-$ for palladium, resulting in very high repulsion between the palladium complex and negatively charged supports, thus reducing the deposition amount of palladium [31, 32]. Therefore, the palladium loadings are quite low even with high concentration of palladium precursors. Since these three catalysts have almost the same Pd loadings, it is reasonable to predict that they have similar catalytic activities.

Table 4.2.1 Palladium contents on Pd@P25-DP catalysts prepared by deposition-precipitation method.

<i>Catalysts</i>	Pd ^a (wt.%)	Pd ^b (wt.%)
0.5Pd@P25-DP	0.5	0.12
1.0Pd@P25-DP	1.0	0.13
2.0Pd@P25-DP	2.0	0.13

^a Theoretical metal content.

^b Metal content was obtained by ICP.

4.2.2 Temperature Effects

Temperature effects were also investigated over the Pd@P25-DP catalysts. Table 4.2.2 shows the catalytic results of benzyl alcohol oxidation over Pd@P25-DP catalysts conducted at different temperatures. Different from their Pd@P25-IMP counterparts, neither of them have activity at 80 °C, which may be due to the low loadings of catalytic particles. Similarly, apart from benzaldehyde and toluene, there are no other products and with the increase of temperature from 100 to 140 °C, the conversion increases at the expense of benzaldehyde selectivity. Further increase will result in lower conversion with higher selectivity. From figure 4.2.3, it can be seen these three have almost the same activity towards benzyl alcohol transformation, which confirms our aforementioned prediction. Interestingly, the maximum conversion as well as the lowest aldehyde selectivity are reached at 140 °C, compared to 120 °C for Pd@P25-IMP catalysts. However, due to less active sites resulting from low metal loadings, the conversion of benzyl alcohol is much smaller than that of their Pd@P25-IMP counterparts with slightly higher aldehyde selectivity for all three at all temperature ranges.

Cao proposed that the oxidative reaction and disproportionation have different active sites, with metal sites for former reaction and metal-support interface for the latter one [23]. Therefore, the higher aldehyde selectivity may be due to relative increase of metal active sites towards metal-support interface sites, although both of them have dramatically decreased compared to Pd@P25-IMP catalysts.

Table 4.2.2 Catalytic results of benzyl alcohol oxidation over Pd@P25-DP catalysts at different temperatures.

Catalyst	Temperature °C	Conversion (%)	Selectivity (%)	
			Benzaldehyde	Toluene
0.5Pd@P25-DP	80	0	0	0
0.5Pd@P25-DP	100	2.9	97.7	2.3
0.5Pd@P25-DP	120	12.2	79.1	20.9
0.5Pd@P25-DP	140	22.5	71.5	28.5
0.5Pd@P25-DP	160	15.8	84.0	16.0
1.0Pd@P25-DP	80	0	0	0
1.0Pd@P25-DP	100	3.3	98.8	1.2
1.0Pd@P25-DP	120	12.3	87.1	12.9
1.0Pd@P25-DP	140	20.2	74.6	25.4
1.0Pd@P25-DP	160	14.6	87.0	13.0
2.0Pd@P25-DP	80	0	0	0
2.0Pd@P25-DP	100	3.0	100	0
2.0Pd@P25-DP	120	13.7	86.3	13.7
2.0Pd@P25-DP	140	19.4	74.6	25.4
2.0Pd@P25-DP	160	17.6	87.6	12.4

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

min⁻¹; reaction time, 1h.

4.2.3 Reaction Duration Effects

Table 4.2.3 shows the catalytic results of benzyl alcohol oxidation over Pd@P25-DP catalysts for different reaction durations at 140 °C, the optimum temperature for Pd@P25-DP catalysts. It can be seen, as the reaction proceeds, the selectivity towards aldehyde is increasing for all of the three catalysts, implying the oxidative path precedes the disproportionation one. Compared to their Pd@P25-IMP counterparts, less than 60%

of the converted benzyl alcohol transformed into aldehyde in the first 0.5 hour through the disproportionation path, while more than 40% of them are oxidized into benzaldehyde by oxygen, implying the oxidation path exceeds the disproportion path in a shorter time. As a result, much higher aldehyde selectivity are obtained with the increase of reaction time. The continuous increase of conversion also prove the excellence of deposition-precipitation method in preparing catalysts with high stability.

Table 4.2.3 Catalytic results of benzyl alcohol oxidation over Pd@P25-DP catalysts for different reaction durations.

Catalysts	Reaction Time (h)	Conversion (%)	Selectivity (%)	
			Benzaldehyde	Toluene
0.5Pd@P25-DP	0.5	9.5	69.9	30.1
0.5Pd@P25-DP	1.0	22.5	71.5	28.5
0.5Pd@P25-DP	2.0	34.5	77.0	23.0
0.5Pd@P25-DP	4.0	47.6	89.2	10.8
1.0Pd@P25-DP	0.5	11.9	70.3	29.7
1.0Pd@P25-DP	1.0	20.2	74.6	25.4
1.0Pd@P25-DP	2.0	37.2	82.3	17.7
1.0Pd@P25-DP	4.0	51.8	87.9	12.1
2.0Pd@P25-DP	0.5	9.2	74.6	25.4
2.0Pd@P25-DP	1.0	19.4	74.6	25.4
2.0Pd@P25-DP	2.0	23.3	94.1	5.9
2.0Pd@P25-DP	4.0	37.9	96.3	3.7

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

4.2.4 Catalyst/Substrate Weight Ratio Effects

Table 4.2.4 shows the catalytic results of benzyl alcohol oxidation over Pd@P25-DP catalysts at different catalysts/substrate ratios. Similar to their Pd@P25-IMP counterparts, the substrate can be transformed in the highest selectivity towards aldehyde with quite low conversion when 5 mg of catalysts are used. With the increase of the amount of catalysts from 5 to 10 mg, the aldehyde selectivity gradually decrease due to the accumulation of toluene resulting from the preceding disproportionation reaction. When the amount of catalysts are further increased, the aforementioned relative high ratio of metal active sites to metal-support interface sites and the accumulation of toluene result a slightly higher conversion. Mass transfer problems also occur when the amount of catalysts is increased from 20 mg to 40 mg.

Table 4.2.4 Catalytic results of benzyl alcohol oxidation over Pd@P25-DP catalysts at different catalysts/substrate ratios.

Catalysts	Weight of Catalysts (mg)	Conversion (%)	Selectivity (%)	
			Benzaldehyde	Toluene
0.5Pd@P25-DP	5	6.6	86.0	14.0
0.5Pd@P25-DP	10	15.0	71.6	28.4
0.5Pd@P25-DP	20	22.5	71.5	28.5
0.5Pd@P25-DP	40	16.9	76.8	23.2
1.0Pd@P25-DP	5	6.2	96.6	3.4
1.0Pd@P25-DP	10	15.5	73.2	26.8
1.0Pd@P25-DP	20	20.2	74.6	25.4
1.0Pd@P25-DP	40	16.8	78.7	21.3
2.0Pd@P25-DP	5	7.4	88.6	11.4
2.0Pd@P25-DP	10	16.5	80.0	20.0
2.0Pd@P25-DP	20	17.6	87.6	22.4
2.0Pd@P25-DP	40	14.5	88.0	12.0

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

4.2.5 Oxygen Flow Rate Effects

Table 4.2.5 shows the catalytic results of benzyl alcohol oxidation over Pd@P25-DP catalysts at different oxygen flow rates. Similar to their Pd@P25-IMP counterparts, no deeper oxidative products or other byproducts are obtained in the whole range of 5 mL min⁻¹ to 40 mL min⁻¹, suggesting the excellent controllability of these catalytic systems in inhibiting deep oxidative reactions. With the increase of oxygen flow rate, both the aldehyde selectivity and conversion are improving at the same time.

Table 4.2.5 Oxygen flow rate effects on benzyl alcohol oxidation over Pd@P25-DP catalysts.

Catalysts	Oxygen Flow Rate (mL min ⁻¹)	Conversion (%)	Selectivity (%)	
			Benzaldehyde	Toluene
0.5Pd@P25-DP	5	14.6	69.2	30.8
0.5Pd@P25-DP	10	22.3	68.3	31.7
0.5Pd@P25-DP	20	22.5	71.5	28.5
0.5Pd@P25-DP	40	22.5	69.8	30.2
1.0Pd@P25-DP	5	11.5	65.9	34.1
1.0Pd@P25-DP	10	19.0	69.7	30.3
1.0Pd@P25-DP	20	20.2	74.6	25.4
1.0Pd@P25-DP	40	20.9	76.9	23.1
2.0Pd@P25-DP	5	12.2	79.5	20.5
2.0Pd@P25-DP	10	15.7	82.8	19.7
2.0Pd@P25-DP	20	17.6	87.6	12.4
2.0Pd@P25-DP	40	19.6	87.8	12.2

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

4.3 Pd@TNW-IMP Catalysts for Benzyl Alcohol Oxidation

The XRD patterns of titanium dioxide nanowires as well as standard rutile and anatase are shown in Figure 4.3.1. The diffraction peaks at 2θ of 27.5°, 36.1°, 39.2°, 41.2°, 44.1°, 54.3°, 56.6°, 56.6°, 62.7°, 64.0°, 69.0°, 69.8° are attributed to the (110), (101), (200), (111), (210), (211), (220), (002), (211), (310), (301), (112) facets of rutile titanium dioxide. There are no anatase phase peaks observed, suggesting the good crystallinity of titanium dioxide nanowires. The morphologies of titanium dioxide nanowires are further investigated by FESEM techniques. Figure 4.3.2 shows the typical SEM images of TNW nanomaterial.

Figure 4.3.1 XRD patterns of titanium dioxide nanowire, standard rutile (green line) and standard anatase (red line) titanium dioxide.

Figure 4.3.2 FESEM images of titanium dioxide nanowires.

It can be seen that nanowires with about 100 nm in diameter and several to dozens of micrometers in length are formed through the molten-salt flux method using commercial available P25, sodium chloride and sodium phosphate dibasic. No P25 nanoparticles are observed, suggesting the complete transformation of P25 to titanium dioxide nanowires. In the following sections, they are being used as supporting material to load palladium catalysts for the aerobic solvent-free selective oxidation of benzyl alcohol.

4.3.1 Characterization of Pd@TNW-IMP catalysts

Figure 4.3.3 shows the XRD patterns of a series of palladium catalysts supported on titanium dioxide nanowires prepared by an incipient wetness impregnation method as well as that of TNW. Similar to the XRD patterns of Pd@P25-IMP catalysts, apart from the intense peaks attributed to TNW nanostructures, no discernable peaks of palladium are observed even for 2.0 wt.% palladium catalysts, suggesting that the palladium nanostructures are highly dispersed on the titanium dioxide nanostructures. The dispersion of nanostructures was further investigated by TEM, and the results are illustrated Figure 4.3.4.

Figure 4.3.3 XRD patterns of titanium dioxide nanowires (TNW), 0.5Pd@TNW-IMP, 1.0Pd@TNW-IMP, and 2.0Pd@TNW-IMP catalysts.

Figure 4.3.4 TEM images and Pd particle size distributions of 2.0Pd@TNW-IMP catalysts.

Due to the high temperature employed in the nanowire synthesis procedure, most of the surface functional groups are eliminated, leaving smooth surfaces both structurally and chemically. Therefore, the interactions between Pd complexes and supporting materials are quite weak and much larger Pd nanoparticles should be formed on titanium dioxide nanowires compared to those formed on P25 nanoparticles. Figure 4.3.4 shows the TEM images and Pd particle size distributions of 2.0Pd@TNW-IMP catalysts. It can be seen from the image that titanium dioxide nanostructures are nanowires with a diameter of around 100 nm and dozens of micrometers in length while Pd catalysts show a mean particle size at around 10 nm with a broad size distribution, verifying our aforesaid prediction. However, given enough time, higher Pd loadings are achievable. The metal loadings of palladium on Pd@TNW-IMP catalysts are shown on Table 4.3.1. Nearly 80% of the palladium precursors are deposited on the TNW supporting material for 1.0Pd@TNW-IMP and 2.0Pd@TNW-IMP catalysts with only 40% of them for

0.5Pd@TNW-IMP, which are slightly lower compared to their Pd@P25-IMP counterparts.

Table 4.3.1 Palladium contents on Pd@TNW-IMP catalysts prepared by wetness impregnation method.

Catalysts	Pd ^a (wt.%)	Pd ^b (wt.%)
0.5Pd@TNW-IMP	0.5	0.21
1.0Pd@TNW-IMP	1.0	0.78
2.0Pd@TNW-IMP	2.0	1.67

^a Theoretical metal content.

^b Metal content was obtained by ICP.

4.3.2 Temperature Effects

Temperature effects were also investigated over the Pd@TNW-IMP catalysts. Table 4.3.2 shows the catalytic results of benzyl alcohol oxidation over Pd@TNW-IMP catalysts conducted at different temperatures. Different from their Pd@P25-IMP counterparts, neither of oxidative nor disproportionation reactions occurs at 80 °C. As the palladium particle size and total metal loadings of them are comparable to that of Pd@P25-IMP catalysts, a proper explanation is the metal-support interactions. With the increase of temperature, more substrates are converted into aldehydes. Astonishingly, there are no other products like toluene or deeper oxidative products, even when the temperature is elevated to 160 °C. In other words, the common disproportionation process is completely inhibited as a result of TNW supporting material. This may be

due to the fact that after high temperature annealing, there are few defects and surface functional groups among TNW compared to its precursor – P25. Therefore, disproportionation reactions resulting from metal-support interface sites are completely suppressed. Despite 100% selectivity towards aldehydes, the conversion is quite low compared to their Pd@P25-IMP counterparts, with only 15% of reactants transformed after 1 hour reaction because of fewer active sites.

Table 4.3.2 Catalytic results of benzyl alcohol oxidation over Pd@TNW-IMP catalysts at different temperatures.

Catalysts	Temperature °C	Conversion (%)	Selectivity (%)	
			Benzaldehyde	Toluene
0.5Pd@TNW-IMP	80	0	0	0
0.5Pd@TNW-IMP	100	1.1	100	0
0.5Pd@TNW-IMP	120	7.6	100	0
0.5Pd@TNW-IMP	140	12.8	100	0
0.5Pd@TNW-IMP	160	14.3	100	0
1.0Pd@TNW-IMP	80	0	0	0
1.0Pd@TNW-IMP	100	1.9	100	0
1.0Pd@TNW-IMP	120	9.9	100	0
1.0Pd@TNW-IMP	140	11.6	100	0
1.0Pd@TNW-IMP	160	14.4	100	0
2.0Pd@TNW-IMP	80	0	0	0
2.0Pd@TNW-IMP	100	1.7	100	0
2.0Pd@TNW-IMP	120	9.4	100	0
2.0Pd@TNW-IMP	140	11.2	100	0
2.0Pd@TNW-IMP	160	14.4	100	0

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

time, 1h.

4.3.3 Reaction Duration Effects

Table 4.3.3 shows the catalytic results of benzyl alcohol oxidation over Pd@TNW-IMP catalysts for different reaction durations at 160 °C, the optimum temperature for Pd@TNW-IMP catalysts. It can be seen, the conversion is gradually increasing with reaction time and apart from benzaldehyde no other products are produced, even after four hours of reaction, implying the excellent aldehyde selectivity and stability of Pd@TNW-DP catalysts.

Table 4.3.3 Catalytic results of benzyl alcohol oxidation over Pd@TNW-IMP catalysts for different reaction durations.

Catalysts	Reaction Time (h)	Conversion (%)	Selectivity (%)	
			Benzaldehyde	Toluene
0.5Pd@TNW-IMP	0.5	7.1	100	0
0.5Pd@TNW-IMP	1.0	14.3	100	0
0.5Pd@TNW-IMP	2.0	20.7	100	0
0.5Pd@TNW-IMP	4.0	25.0	100	0
1.0Pd@TNW-IMP	0.5	7.1	100	0
1.0Pd@TNW-IMP	1.0	14.4	100	0
1.0Pd@TNW-IMP	2.0	22.9	100	0
1.0Pd@TNW-IMP	4.0	34.1	100	0
2.0Pd@TNW-IMP	0.5	7.8	100	0
2.0Pd@TNW-IMP	1.0	14.4	100	0
2.0Pd@TNW-IMP	2.0	19.4	100	0
2.0Pd@TNW-IMP	4.0	28.7	100	0

^a Reaction conditions: catalyst, 20 mg; benzyl alcohol, 50 mmol; O₂, 20 mL min⁻¹; temperature, 160 °C.

4.3.4 Catalyst/Substrate Weight Ratio Effects

Table 4.3.4 shows the catalytic results of benzyl alcohol oxidation over Pd@TNW-IMP catalysts at different catalysts/substrate ratios. As seen from the table and figure, 100% selectivity towards benzaldehyde is maintained with the increase of catalysts from 5 to 40 mg. Similar to the their aforementioned counterparts, mass transfer problems occur when the amount of catalysts was further increased from 20 to 40 mg, resulting slightly lower conversion.

Table 4.3.4 Catalytic results of benzyl alcohol oxidation over Pd@TNW-IMP catalysts at different catalysts/substrate ratios.

Catalysts	Weight of Catalysts (mg)	Conversion (%)	Selectivity (%)	
			Benzaldehyde	Toluene
0.5Pd@TNW-IMP	5	7.3	100	0
0.5Pd@TNW-IMP	10	9.5	100	0
0.5Pd@TNW-IMP	20	14.3	100	0
0.5Pd@TNW-IMP	40	12.6	100	0
1.0Pd@TNW-IMP	5	8.6	100	0
1.0Pd@TNW-IMP	10	10.8	100	0
1.0Pd@TNW-IMP	20	14.4	100	0
1.0Pd@TNW-IMP	40	13.4	100	0
2.0Pd@TNW-IMP	5	5.4	100	0
2.0Pd@TNW-IMP	10	10.0	100	0
2.0Pd@TNW-IMP	20	14.4	100	0
2.0Pd@TNW-IMP	40	14.1	100	0

^a Reaction conditions: benzyl alcohol, 50mmol; O₂, 20mL min⁻¹; time, 1h; temperature, 160 °C.

4.3.5 Oxygen Flow Rate Effects

Table 4.3.5 shows the catalytic results of benzyl alcohol oxidation over Pd@TNW-IMP catalysts at different oxygen flow rates. Similar to their aforementioned counterparts, no further oxidative products like acids are obtained even when the oxygen rate was increased from 5 to 40 mL min⁻¹. The catalysts are capable of keeping 100% aldehyde selectivity throughout the range, suggesting the excellent controllability of these catalytic systems in inhibiting deeper oxidative reactions. Similar results for conversion are obtained. That is, when the oxygen flow rate was increased from 5 to 20 mL min⁻¹, more alcohol are converted while the conversion is becoming lower when 40 mL min⁻¹ of oxygen was bubbled into the system due to mass transfer problems.

Table 4.3.5 Catalytic results of benzyl alcohol oxidation over Pd@TNW-IMP catalysts at different oxygen flow rates.

Catalysts	Oxygen Flow Rate (mL min ⁻¹)	Conversion (%)	Selectivity (%)	
			Benzaldehyde	Toluene
0.5Pd@TNW-IMP	5	5.2	100	0
0.5Pd@TNW-IMP	10	6.9	100	0
0.5Pd@TNW-IMP	20	14.3	100	0
0.5Pd@TNW-IMP	40	10.4	100	0
1.0Pd@TNW-IMP	5	9.3	100	0
1.0Pd@TNW-IMP	10	10.0	100	0
1.0Pd@TNW-IMP	20	14.4	100	0
1.0Pd@TNW-IMP	40	11.1	100	0
2.0Pd@TNW-IMP	5	9.4	100	0
2.0Pd@TNW-IMP	10	10.1	100	0
2.0Pd@TNW-IMP	20	14.4	100	0
2.0Pd@TNW-IMP	40	13.2	100	0

^a Reaction conditions: catalyst, 20 mg; benzyl alcohol, 50 mmol; time, 1h; temperature, 160 °C.

4.4 Pd@TNW-DP Catalysts for Benzyl Alcohol Oxidation

4.4.1 Characterization of Pd@TNW-DP Catalysts

Figure 4.4.1 XRD patterns of titanium dioxide nanowires (TNW), 0.5Pd@TNW-DP, 1.0Pd@TNW-DP, and 2.0Pd@TNW-DP catalysts.

Figure 4.4.1 shows the XRD patterns of a series of palladium catalysts supported on titanium dioxide nanowires prepared by a deposition-precipitation method as well as that of TNW. Similar to the XRD patterns of Pd@TNW-IMP catalysts, apart from the intense peaks attributed to TNW nanostructures, no discernable peaks of palladium are observed even for 2.0 wt.% palladium catalysts, suggesting that the palladium

nanostructures are highly dispersed on the titanium dioxide nanostructures. The dispersion of nanostructures was further investigated by TEM, and the results are illustrated Figure 4.4.2.

Figure 4.4.2 TEM images of 2.0Pd@TNW-DP catalysts.

As shown in Figure 4.4.2, palladium nanoparticles with a diameter around 14.5 nm are deposited on the surface of TNW supporting material. As very few particles are observed, it's very difficult to obtain the size distributions. The thinner particles in the image may indicate the lower metal loadings compared to that of their 2.0Pd@TNW-IMP counterparts. The hypothesis is confirmed by the metal contents obtained by ICP. It can be seen only about 50% of the palladium precursors are readily deposited on the support while it's much higher than their Pd@P25-DP catalysts due to less hydroxyl groups on the nanowires resulting from high temperature calcination.

Table 4.4.1 Palladium contents on Pd@TNW-DP catalysts prepared by deposition-precipitation method.

Catalysts	Pd ^a (wt.%)	Pd ^b (wt.%)
0.5Pd@TNW-DP	0.5	0.21
1.0Pd@TNW-DP	1.0	0.53
2.0Pd@TNW-DP	2.0	0.99

^a Theoretical metal content.

^b Metal content was obtained by ICP.

4.4.2 Temperature Effect

Table 4.4.2 shows the catalytic results of benzyl alcohol oxidation over Pd@TNW-DP catalysts conducted at different temperatures. Similar to its Pd@TNW-IMP counterparts, neither of oxidative nor disproportionation reactions occurs at 80 °C. With the increase of temperature, more substrates are converted into aldehyde with almost 100% selectivity towards aldehyde. The only exception, 2.0Pd@TNW-DP, transforms quite a few alcohols into toluene when the temperature is in the range of 140 and 160 °C. The suppression of disproportionation path over Pd@TNW-DP catalysts further prove the excellent property of TNW as a supporting material. Also, the conversion is quite low compared to their Pd@P25-IMP counterparts, with only around 17% of reactants transformed after 1 hour reaction for 2.0Pd@TNW-DP catalysts.

Table 4.4.2 Catalytic results of benzyl alcohol oxidation over Pd@TNW-DP catalysts at different temperatures.

Catalysts	Temperat °C	Conversion (%)	Selectivity (%)	
			Benzaldehyde	Toluene

0.5Pd@TNW-DP	80	0	0	0
0.5Pd@TNW-DP	100	2.1	100	0
0.5Pd@TNW-DP	120	8.1	100	0
0.5Pd@TNW-DP	140	10.9	100	0
0.5Pd@TNW-DP	160	12.3	100	0
1.0Pd@TNW-DP	80	0	0	0
1.0Pd@TNW-DP	100	3.7	100	0
1.0Pd@TNW-DP	120	9.0	100	0
1.0Pd@TNW-DP	140	10.7	100	0
1.0Pd@TNW-DP	160	13.4	100	0
2.0Pd@TNW-DP	80	0	0	0
2.0Pd@TNW-DP	100	4.7	100	0
2.0Pd@TNW-DP	120	10.5	100	0
2.0Pd@TNW-DP	140	12.1	99.4	0.6
2.0Pd@TNW-DP	160	17.8	98.6	1.4

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

4.4.3 Reaction Duration Effects

Table 4.4.3 shows the catalytic results of benzyl alcohol oxidation over Pd@TNW-DP catalysts for different reaction durations at 160 °C, the optimum temperature for Pd@TNW-DP catalysts. It can be seen, for 0.5Pd@TNW-DP and 1.0Pd@TNW-DP catalysts, the conversion is gradually increasing with reaction time and apart from benzaldehyde no other products are produced, even after four hours of reaction, implying the excellent aldehyde selectivity and stability of Pd@TNW-DP catalysts. For 2.0Pd@TNW-DP catalysts, slight toluene are obtained as byproduct and with the reaction time, the selectivity towards aldehyde is increasing until 100% selectivity is reached after 4 hours. Confirmed by the first two sections of this chapter, catalysts

prepared by deposition-precipitation method usually have a better performance in aldehyde selectivity than that synthesized by incipient wetness impregnation method. While for Pd@TNW-IMP catalysts, 100% selectivity are maintained throughout all series of parameters tested, the slight deviation of 2.0Pd@TNW-DP catalysts may be due to larger particle size than 2.0Pd@TNW-IMP catalysts (14.5 vs. 10.0 nm).

Table 4.4.3 Catalytic results of benzyl alcohol oxidation over Pd@TNW-DP catalysts for different reaction durations.

Catalysts	Reaction Time (h)	Conversion (%)	Selectivity (%)	
			Benzaldehyde	Toluene
0.5Pd@TNW-DP	0.5	7.9	100	0
0.5Pd@TNW-DP	1.0	12.3	100	0
0.5Pd@TNW-DP	2.0	20.8	100	0
0.5Pd@TNW-DP	4.0	36.5	100	0
1.0Pd@TNW-DP	0.5	7.9	100	0
1.0Pd@TNW-DP	1.0	13.4	100	0
1.0Pd@TNW-DP	2.0	19.0	100	0
1.0Pd@TNW-DP	4.0	29.9	100	0
2.0Pd@TNW-DP	0.5	9.8	98.0	2.0
2.0Pd@TNW-DP	1.0	17.8	98.6	1.4
2.0Pd@TNW-DP	2.0	25.7	99.4	0.6
2.0Pd@TNW-DP	4.0	30.6	100	0

^a Reaction conditions: catalyst, 20 mg; benzyl alcohol, 50mmol; O₂, 20mL min⁻¹; temperature, 160 °C.

4.4.4 Catalyst/Substrate Weight Ratio Effects

Table 4.4.4 shows the catalytic results of benzyl alcohol oxidation over Pd@TNW-DP catalysts at various catalysts/substrate ratios. As seen from the table and figure, 100%

selectivity towards benzaldehyde is maintained with the increase of catalysts from 5 to 40 mg for 0.5Pd@TNW-DP and 1.0Pd@TNW-DP catalysts, while the aldehyde selectivity is gradually increasing for 2.0Pd@TNW-DP catalysts within the range of 5 to 20 mg. Similar to the their aforementioned counterparts, mass transfer problems occur when the amount of catalysts was further increased from 20 to 40 mg, resulting in slightly lower conversion for the three catalysts and poor aldehyde selectivity for 2.0Pd@TNW-DP catalysts.

Table 4.4.4 Catalytic results of benzyl alcohol oxidation over Pd@TNW-DP catalysts at different catalysts/substrate ratios.

Catalysts	Weight of Catalysts (mg)	Conversion (%)	Selectivity (%)	
			Benzaldehyde	Toluene
0.5Pd@TNW-DP	5	9.9	100	0
0.5Pd@TNW-DP	10	12.5	100	0
0.5Pd@TNW-DP	20	12.3	100	0
0.5Pd@TNW-DP	40	12.2	100	0
1.0Pd@TNW-DP	5	11.4	100	0
1.0Pd@TNW-DP	10	12.1	100	0
1.0Pd@TNW-DP	20	13.4	100	0
1.0Pd@TNW-DP	40	14.6	100	0
2.0Pd@TNW-DP	5	13.1	94.9	5.1
2.0Pd@TNW-DP	10	17.7	96.7	3.3
2.0Pd@TNW-DP	20	17.8	98.6	1.4
2.0Pd@TNW-DP	40	12.3	97.8	2.2

^a Reaction conditions: benzyl alcohol, 50 mmol; O₂, 20 mL min⁻¹; time, 1h; temperature, 160 °C.

4.4.5 Oxygen Flow Rate Effects

Table 4.4.5 shows the catalytic results of benzyl alcohol oxidation over Pd@TNW-DP catalysts at different oxygen flow rates. Similar to their aforementioned counterparts, no further oxidative products like benzoic acid are obtained even when the oxygen rate was increased from 5 to 40 mL min⁻¹. For 0.5Pd@TNW-DP and 1.0Pd@TNW-DP catalysts, the catalysts are capable of keeping 100% aldehyde selectivity throughout the range, suggesting the excellent controllability of these catalytic systems in inhibiting deep oxidative reactions while for 2.0Pd@TNW-DP catalysts, the aldehyde selectivity is continuously increasing with the increase of oxygen flow rate. Similar results for conversion are obtained. That is, when the oxygen flow rate was increased from 5 to 20 mL min⁻¹, more alcohol are converted while the conversion is becoming lower when 40 mL min⁻¹ of oxygen was bubbled into the system due to mass transfer problems.

Table 4.4.5 Catalytic results of benzyl alcohol oxidation over Pd@TNW-DP catalysts at different oxygen flow rates.

Catalysts	Oxygen Flow Rate (mL min ⁻¹)	Conversion (%)	Selectivity (%)	
			Benzaldehyde	Toluene
0.5Pd@TNW-DP	5	7.6	100	0
0.5Pd@TNW-DP	10	9.4	100	0
0.5Pd@TNW-DP	20	12.3	100	0
0.5Pd@TNW-DP	40	15.1	100	0
1.0Pd@TNW-DP	5	9.0	100	0
1.0Pd@TNW-DP	10	13.2	100	0
1.0Pd@TNW-DP	20	13.4	100	0
1.0Pd@TNW-DP	40	9.6	100	0
2.0Pd@TNW-DP	5	12.5	90.3	9.7
2.0Pd@TNW-DP	10	12.1	93.7	6.3
2.0Pd@TNW-DP	20	17.8	98.6	1.4

^a Reaction conditions: catalyst, 20 mg; benzyl alcohol, 50 mmol; time, 1h; temperature, 160 °C.

Discussion

Figure 4.5.1 Effects of supports and preparation methods on the benzyl alcohol conversion. Reaction conditions: catalyst, 20 mg; benzyl alcohol, 50mmol; O₂, 20mL min⁻¹; temperature, optimum temperature for each one.

For all the catalysts, benzaldehyde and toluene are the only products in the aerobic oxidation of benzyl alcohol. However, due to the variation in preparation methods and supporting materials, they have quite different activities and aldehyde selectivity. Although it's unreasonable to compare the performances of these catalysts for benzyl

alcohol oxidation under different reaction temperatures, we can still have a deeper understanding by examining the best results we can get from these catalysts. Also, Pd@P25-DP catalysts have very low and similar loadings; therefore only the other three catalysts are being compared. Figure 4.5.1 shows the change of activity of each catalysts with metal loadings, which is obtained at its optimum temperature while other parameters are kept the same.

It can be seen Pd@P25-IMP catalysts have the best catalytic activity with same metal loadings, which can be attributed to smaller particle sizes and abundance of hydroxyl groups on P25 acting as promoters in benzyl alcohol transformation. Also, the metal loadings have less influence on the catalysts prepared by impregnation method, suggesting 0.5 wt.% loadings is enough for them to be saturated in the present catalytic system. However, a further loading on TNW using a DP method might be able to increase the activity further more.

Figure 4.5.2 shows the change of aldehyde selectivity of each catalysts with metal loadings, which is also obtained at its optimum temperature while other parameters are kept the same. It is obvious that catalysts based on TNW have almost 100% selectivity towards aldehyde, while quite a lot of toluene are produced for catalysts based on P25, suggesting the excellent ability of titanium dioxide nanowires in inhibition of disproportionation path. Therefore, further modification of TNW-based catalysts with

high activity have the potential to be used in large-scale synthesis of benzaldehyde through benzyl alcohol oxidation.

Figure 4.5.2 Effects of supports and preparation methods on the benzaldehyde selectivity. Reaction conditions: catalyst, 20 mg; benzyl alcohol, 50mmol; O₂, 20mL min⁻¹; temperature, optimum temperature for each one.

Summary

A series of palladium catalysts supported on commercial available titanium dioxide nanoparticles and titanium dioxide nanowires synthesized by a molten salt flux method are prepared by two common methods, urea-assisted deposition-precipitation and incipient wetness impregnation methods. Selective oxidation of benzyl alcohol was employed as a model reaction to investigate the performance of as-prepared catalysts. It is found that catalysts prepared by the impregnation method have larger metal

loadings with a broader size distribution than that prepared by the deposition-precipitation method, resulting in much higher activity with lower selectivity towards benzaldehyde. The lower loadings of palladium nanoparticles using deposition-precipitation method was due to the greater repulsion between support materials and palladium complex at elevated pH. The influences of reaction parameters including reaction temperature, reaction duration, catalysts/substrate molar ratio and oxygen flow rate are studied. For all the catalysts, benzyl alcohol can be transformed by two seemingly independent routes, one of which results in the production of toluene and equimolar amounts of benzaldehyde as well as water while the other produces only benzaldehyde and water. No further oxidative compounds are obtained, suggesting the excellent controllability of as-prepared catalysts in inhibiting deeper oxidation reaction. It is believed initially only the disproportionation route is active and as time proceeds, the oxidation reaction is triggered, gradually match and finally exceeds the disproportionation route. Due to the existence of mass transfer problems, all of them have their own optimum reaction parameters for catalysts/substrate weight ratio and oxygen flow rates. Also, catalytic results showed that water is the main reason for catalysts deactivation and removal of the toluene produced at early stages in time might be able to fully inhibit the disproportion route, resulting in almost 100% selectivity towards aldehyde. Although catalysts based on titanium dioxide nanoparticles have better activity compared to their nanowire counterparts, much lower aldehyde selectivity is its main disadvantage. With 100% selective towards benzaldehyde and excellent stability, further modification of palladium catalysts supported on titanium

dioxide nanowire have the potential to be used in large-scale synthesis of benzaldehyde through benzyl alcohol oxidation.

List of abbreviations

IMP	Incipient Wetness Impregnation
DP	Urea-assisted Deposition-Precipitation
ICP	Inductively coupled plasma
TEM	Transmission Electron Microscopy
SEM	Scanning Electron Microscope
XRD	X-Rays Diffraction
TNW	Titanium Dioxide Nanowires

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Chapter 5 Palladium Catalysts Supported On Nitrogen-Doped Carbon

Nanotubes for Benzyl Alcohol Oxidation

Doping carbon nanotubes with heteroatoms like boron [1], nitrogen [2-4], phosphine [5], sulfur [6], and halogens [7-9] have been proved efficient ways to modify their structural and electronical properties. Among them, nitrogen has been extensively studied due to its size proximity to carbon and a lot of methods have been developed and improved to control the doping process. Apart from the amounts of dopants, another important factor is the way foreign atoms like nitrogen are incorporated into the tubular system. Nitrogen atoms can directly substitute carbon atoms to form the quaternary bonding without changing the wall configuration; it can also form the pyridinic type of bonding, even a third type of pyrrolic type of bonding system [4, 10]. Either way, local electronic properties will be changed because of the doped nitrogen atom, having one more electron than carbon atom. As a result, metal ions like platinum [11, 12], ruthenium [13] are more favorable to absorb on the surface of nitrogen-doped carbon nanotubes than that of pure carbon nanotubes. Moreover, base sites introduced by pyridinic nitrogen atoms are capable of catalyzing dehydrogenation reactions [14] and transition metal catalysts supported on such extraordinary materials are believed to have better performance in base catalyzed reactions.

Most techniques to synthesize nitrogen-doped carbon nanotubes employ similar approaches to produce carbon nanotubes except appropriate nitrogen sources such as nitrogen gas [15], ammonia [16], organic amines are added into reaction system. Although various amounts of nitrogen as low as 1% and as high as 20% have been successfully doped into the carbon nanotube skeletons, these methods either require

high temperature or noxious compounds, which is energy-waste and unsafe [4, 17]. Furthermore, carbon allotropes including amorphous carbon are sometimes present as impurity, which affords subsequent tedious and time-consuming purification steps [18]. Considering carbon nanotubes are concentric tubes rolled by one or a few graphene planes, similar ways that are used to dope nitrogen into graphene layers might be applicable to obtain nitrogen-doped carbon nanotubes. Therefore, in this chapter, several nitrogen sources including hydrazine combined with ammonia [19, 20], urea [21], hexamethylenetetramine [22], dicyandiamide [23], and hydroxylamine chloride [24] that have been employed to prepare nitrogen-doped graphene are used to modify carbon nanotubes under a simple hydrothermal condition. Then these obtained nanotubes will be used as supporting materials to load palladium catalysts and their performance in solvent-free benzyl alcohol oxidation will be investigated.

5.1 Characterization of Nitrogen-doped Carbon Nanotubes

Figure 5.1.1 shows the XRD patterns of pristine CNT and nitrogen-doped CNT prepared with different nitrogen sources. The strong (002) diffraction of hexagonal graphite at 2θ of 26.2° suggests that the graphite structure of CNTs is retained after oxidizing and purifying CNTs in concentric nitric acid at 120°C for 6 hours. Furthermore, the less strong peak at 43.3° can be attributed to the (100) facets of CNT. Nitrogen-doped CNT with different nitrogen sources are also compared to that of CNTs. Apart from the XRD peaks at 26.02° and 43.3° , no other peaks are observed, which is in good agreement with the results reported by Dong et al. Nitrogen doping can only increase the disorder of carbon nanotubes, resulting in the decrease of peak intensities, no additional peaks can be found attributed to the dopant [25].

Figure 5.1.1 XRD patterns of CNT and nitrogen-doped CNT with different nitrogen sources.

As a well-developed technique to characterize various carbon materials in the last four decades, Raman spectroscopy has been widely used to give structural information including the introduction of foreign atoms, defects and many others [26]. Figure 5.1.2 shows the Raman spectra of CNT and nitrogen-doped CNT with different nitrogen sources. In the first-order range, two strong peaks are present for both pristine and nitrogen-doped carbon nanotubes. The first band or D band, centered at 1345 cm^{-1} , is often used as an indicator of extent of disorder [10] while G band, situated at 1578 cm^{-1} , arises from an E_{2g} vibrational mode and is a characteristic band for all sp^2 carbon materials [27]. The intensity ratio of D band and G band (I_D/I_G) for pure carbon

nanotubes is 0.80, whereas slight increases are observed for nitrogen-doped ones, 0.84 for CNT-N-1, 0.88 for CNT-N-2, 0.86 for CNT-N-3, 0.90 for CNT-N-4, 0.83 for CNT-N-5. Due to the mild reaction conditions, I_D/I_G values more than 1.00 even 2.00 which are common for nitrogen-doped carbon nanotubes prepared by one-step modified CVD methods are very difficult to obtain.

Figure 5.1.2 Raman spectra of CNT and nitrogen-doped CNT with different nitrogen sources.

5.2 Nitrogen Sources' Effects on Benzyl Alcohol Oxidation over Pd@CNT-N Catalysts

The introduction of carbonyl and hydroxyl groups during the purification steps of carbon nanotubes can effectively attract Pd ions in the solution, thus resulting considerable loadings of Pd nanoparticles through the Ionic Absorption-Reduction

method. Similarly, the introduction of various nitrogen atoms can also effectively deposit more Pd ions. Compared to the internal interactions between nitrogen-doped carbon nanotubes with Pd ions, external forces like urea-assisted deposition-precipitation method would deposit noble metal ions less directionally. Therefore, in the following sections, two methods, Ionic Absorption-Reduction and urea-assisted deposition-precipitation methods will be employed to prepare Pd catalysts supported on nitrogen-doped carbon nanotubes and their catalytic performances would be investigated for selective oxidation of benzyl alcohol.

5.2.1 Pd@CNT-N-DP Catalysts Prepared By Deposition-Precipitation Method

Palladium catalysts supported on carbon nanotubes and nitrogen-doped carbon nanotubes were first synthesized through a urea-assisted deposition-precipitation method. Upon heating, urea can be decomposed slowly to produce ammonia and the resulting basic solution will facilitate the deposition of palladium ions on the surface of carbon nanotubes.

Figure 5.2.1.1 shows the XRD patterns of palladium catalysts. Apart from the (002) and (100) facets of carbon nanotubes that are centered at 26.02° and 43.3° respectively, diffraction peaks attributed to palladium are also observed. Strong peaks located at 40.12° can be found on 2Pd@CNT-N-1-DP, 2Pd@CNT-N-3-DP, 2Pd@CNT-N-4-DP, 2Pd@CNT-N-5-DP, which is indexed to (111) facet of palladium. The slightly weaker peak located at 46.6° is (200) facet of palladium nanoparticle. However, no discernable peaks attributed to palladium are available for the other two catalysts, namely, 2Pd@CNT-DP and 2Pd@CNT-N-2-DP, suggesting good dispersability or lower loadings. As urea is employed as a promoter in the deposition and precipitation of

palladium ions for all the supports, similar loadings should be achieved, which were also verified by the ICP measurement.

Figure 5.2.1.1 XRD patterns of palladium catalysts supported on CNT and a series of CNT-N by Urea deposition precipitation method.

Figure 5.2.1.2 TEM graphs and Pd particle size distribution of (a1, a2) 2Pd@CNT-DP; (b1, b2) 2Pd@CNT-N-1-DP; (c1, c2) 2Pd@CNT-N-3-DP.

The as-prepared catalysts are employed to benzyl alcohol oxidation reactions and the catalytic results are shown in Table 5.2.1.1 and Figure 5.2.1.3. It can be seen all the catalysts based on nitrogen-doped supports have higher selectivity towards benzaldehyde compared to that supported on pristine carbon nanotubes. As is known, pyridinic nitrogen can introduce basic sites to carbon nanotubes, which is usually regarded as promoters in cleaving the O-H bond of the alcohol [28]. Therefore, as-

formed base sites can greatly improve the aldehyde selectivity. However, lower or almost the same conversion are obtained due to the omnidirectional deposition of Pd ions on nitrogen-doped carbon nanotubes with poorer crystallinity.

Table 5.2.1.1 Catalytic results of benzyl alcohol oxidation over 2.0Pd@CNT-DP and 2.0Pd@CNT-N-DP catalysts.

Catalysts	Pd ^b (wt.%)	Conversion (%)	Selectivity (%)	
			Benzaldehyde	Toluene
2.0Pd@CNT-DP	1.89	61.0	83.6	16.4
2.0Pd@CNT-N-1-DP	1.85	51.5	92.8	7.2
2.0Pd@CNT-N-2-DP	1.89	65.4	90.5	9.5
2.0Pd@CNT-N-3-DP	1.77	30.2	98.5	1.5
2.0Pd@CNT-N-4-DP	2.01	49.3	93.8	6.2
2.0Pd@CNT-N-5-DP	2.63	44.2	88.2	11.8

^a Reaction conditions: benzyl alcohol, 50 mmol; O₂, 20 mL min⁻¹; time, 3 h; temperature, 160 °C.

^b Metal content was obtained by ICP.

5.2.2 Pd@CNT-N Catalysts Prepared By Ionic Absorption-Reduction Method

Figure 5.2.2.1 shows the XRD patterns of palladium catalysts. Apart from the (002) and (100) facets of carbon nanotubes that are centered at 26.02° and 43.3° respectively, diffraction peaks attributed to palladium are also observed. Strong peaks located at 40.12° can be found on 2Pd@CNT, 2Pd@CNT-N-1, 2Pd@CNT-N-2, 2Pd@CNT-N-3, 2Pd@CNT-N-5, which is indexed to (111) facet of palladium. The slightly weaker peak located at 46.6° is (200) facet of palladium nanoparticle. However, no discernable peaks attributed to palladium are available for the other two catalysts, namely, 2Pd@CNT and 2Pd@CNT-N-4, suggesting good dispersability or lower loadings. The ICP

measurement showed on Table 5.2.2.1 demonstrates that nitrogen-doped carbon nanotubes indeed modify the electronic properties of the tubular system and are more favorable to attract metal ions, resulting large loadings than the pristine ones. Different palladium loadings are observed, suggesting different amounts or types of nitrogen are successfully doped into carbon nanotubes, which might have a profound influence on their catalytic properties.

Figure 5.2.2.1 XRD patterns of palladium catalysts supported on CNT and a series of CNT-N by Absorption-Reduction Method.

Table 5.2.2.1 lists the carbon, nitrogen, hydrogen composition of palladium catalysts supported on pristine carbon nanotubes and those nitrogen-doped ones with different nitrogen sources. Pristine carbon nanotubes have very little nitrogen. However,

upon hydrothermal reaction with various nitrogen sources, nearly tenfold increase is achieved when appropriate nitrogen sources are applied, hexamethylenetetramine for example. As there is no direct relation between the content of nitrogen to that of the listed elements, the doping of nitrogen atoms should be at the expense of oxygen functionalities produced during the purification of carbon nanotubes [29]. The successful doping of nitrogen atoms are expected to tune the electronic properties of carbon nanotubes and therefore influence the catalytic abilities of palladium catalysts.

Table 5.2.2.1 Elemental Composition of Pd catalysts supported on CNT and Nitrogen-doped CNTs.

Samples	C (wt%)	H (wt%)	N (wt%)	N/C (at./at.)
2Pd@CNT	69.56	5.251	0.084	0.121
2Pd@CNT-N-1	67.85	3.505	0.702	1.03
2Pd@CNT-N-2	62.7	6.160	0.650	1.03
2Pd@CNT-N-3	72.42	2.822	0.844	1.16
2Pd@CNT-N-4	57.01	6.308	0.569	0.997
2Pd@CNT-N-5	56.80	5.953	0.159	0.280

The as-prepared catalysts are employed to benzyl alcohol oxidation reactions and the catalytic results are shown in Table 5.2.2.2. It can be seen all the catalysts based on nitrogen-doped supports have both higher conversion and better selectivity towards benzaldehyde compared to that supported on pristine carbon nanotubes, confirming that palladium nanoparticles supported on nitrogen-doped carbon nanotubes indeed have better performance towards alcohol oxidation. For 2Pd@CNT-N-1 and 2Pd@CNT-N-

2 catalysts particularly, a twofold enhancement in benzyl alcohol conversion is obtained compared with only 24% higher catalysts loadings due to the modification of supports' electronic properties by the nitrogen dopants. More attention should be paid to 2.0Pd@CNT-N-5 catalysts, although only 1.76 times more benzyl alcohol conversion is obtained, 100% selectivity towards benzaldehyde can greatly simplify the after-reaction separation procedure. To better understand how the electronic properties are modified, a series of nitrogen-doped carbon nanotubes based on 2.0Pd@CNT-N-5 are synthesized. Different amounts of nitrogen precursors are added to the hydrothermal reaction system, and the as-prepared tubular systems are employed as supports to load palladium catalysts. Their performance on benzyl alcohol oxidation will be investigated and discussed.

Table 5.2.2.2 Catalytic results of benzyl alcohol oxidation over 2.0Pd@CNT and a series of 2.0Pd@CNT-N catalysts prepared by Absorption-Reduction Method.

Catalysts	Pd ^b (wt.%)	Conversion (%)	Selectivity (%)	
			Benzaldehyde	Toluene
2.0Pd@CNT	1.53	26.7	89.1	10.9
2.0Pd@CNT-N-1	1.90	54.3	95.2	4.8
2.0Pd@CNT-N-2	1.90	53.7	93.1	6.9
2.0Pd@CNT-N-3	2.08	29.1	100	0
2.0Pd@CNT-N-4	2.10	32.1	95.0	5.0
2.0Pd@CNT-N-5	1.97	47.2	100	0

^a Reaction conditions: benzyl alcohol, 50 mmol; O₂, 20 mL min⁻¹; time, 3 h; temperature, 160 °C.

^b Metal content was obtained by ICP.

5.3 Effects of Nitrogen Sources/CNT Ratio on the Selective Oxidation of Benzyl Alcohol

Figure 5.3.1 shows the XRD patterns of pristine CNT and nitrogen-doped CNT prepared with different amounts of hydroxylamine chloride added to the hydrothermal reaction system. It can be seen apart from the strong peaks at 26.02° and 43.3° , which can be indexed to the (002) and (100) facets of carbon nanotubes respectively, no other peaks are observed, even when 4.2 g hydroxylamine chloride (weight ratio of hydroxylamine chloride to carbon nanotubes = 14:1) are used, suggesting good retention of the tubular system.

Figure 5.3.1 XRD patterns of CNT and a series of CNT-HACl by Absorption-Reduction Method.

Figure 5.3.2 Raman spectra of CNT and CNT-HACl with different nitrogen sources/CNT ratios.

Figure 5.3.2 shows the Raman spectra of CNT and CNT-HACl prepared with different nitrogen sources/CNT weight ratios. Two strong peaks centered at 1345 cm^{-1} and 1578 cm^{-1} are observed, which can be attributed to D band and G band respectively. With different amounts of hydroxylamine chloride added to the hydrothermal reaction system, different I_D/I_G ratios are obtained. The intensity ratio of D band and G band (I_D/I_G) for pure carbon nanotubes is 0.80, whereas slight increases are observed for nitrogen-doped ones, 0.83 for CNT-HACl-1, 0.88 for CNT-HACl-2, 0.82 for CNT-HACl-3, 0.85 for CNT-HACl-4, 0.83 for CNT-HACl-5 and 0.80 for CNT-HACl-6. It

is interesting the influence of different amounts of hydroxylamine chloride on the modified carbon nanotubes does not change in a regular way, with linear or polynomial increase or decrease. Maybe various types of nitrogen bonding systems are incorporated into the tubular system with different ratios, resulting different extent of modification of the carbon nanotubes. The influence can also be reflected by the XRD patterns, ICP contents and catalytic results below.

Table 5.3.1 lists the carbon, nitrogen and hydrogen composition of Pd catalysts supported on those nitrogen-doped ones prepared with different amounts of nitrogen sources. Similar to the irregular patterns of I_D/I_G ratios, nitrogen contents seem to change randomly with increased amounts of hydroxylamine chloride. Changes in reaction conditions are believed to result in different ratios of various types of nitrogen atoms and thus influence the electronic properties of carbon nanotubes in different ways.

Table 5.3.1 Elemental Composition of Pd catalysts supported on Nitrogen-doped CNTs.

Samples	C (wt%)	H (wt%)	N (wt%)	N/C (at./at.)
2Pd@CNT-HACl-1	66.56	7.902	0.274	0.412
2Pd@CNT-HACl-2	74.07	1.401	0.023	0.0310
2Pd@CNT-HACl-3	68.00	3.959	0.093	0.137
2Pd@CNT-HACl-4	63.37	7.434	0.453	0.715
2Pd@CNT-HACl-5	56.80	5.953	0.159	0.280
2Pd@CNT-HACl-6	65.07	6.038	0.243	0.373

Figure 5.3.3 shows the XRD patterns of palladium catalysts supported on CNT and a series of CNT-HACl supports by Absorption-Reduction Method. Apart from the (002)

and (100) facets of carbon nanotubes that are centered at 26.02° and 43.3° respectively, diffraction peaks attributed to palladium are also observed. Strong peaks located at 40.12° can be found on 2Pd@CNT, 2Pd@CNT-HACl-1, 2Pd@CNT-HACl-2, 2Pd@CNT-HACl-3, 2Pd@CNT-HACl-5 and 2Pd@CNT-HACl-6, which is indexed to (111) facet of palladium. The slightly weaker peak located at 46.6° is (200) facet of palladium nanoparticle. Except these two peaks, another weak one indexed to (220) facet of palladium can also be observed at 68.1° , which is absent for other catalysts supported on carbon nanotubes doped with other nitrogen sources. The influence can also be verified by the ICP measurement. Table 5.3.1 demonstrates that nitrogen-doped carbon nanotubes indeed modify the electronic properties of the tubular system and are more favorable to attract metal ions, resulting larger loadings than the pristine ones. Different palladium loadings are observed, suggesting different amounts or types of

nitrogen are successfully doped into carbon nanotubes, which might have a profound influence on its catalytic properties.

Figure 5.3.3 XRD patterns of palladium catalysts supported on CNT and a series of CNT-HACl supports by Absorption-Reduction Method. a) CNT, b) 2Pd@CNT, c) 2Pd@CNT-HACl-1, d) 2Pd@CNT-HACl-2, e) 2Pd@CNT-HACl-3, f) 2Pd@CNT-HACl-4, g) 2Pd@CNT-HACl-5, h) 2Pd@CNT-HACl-6.

TEM are employed to investigate the evolution of palladium sizes and distribution when nitrogen-doped carbon nanotubes prepared with increased amounts of hydroxylamine chloride are used as supporting materials and the typical images are shown in Figure 5.3.4. The mass of carbon nanotubes are fixed to 300 mg and increasing

mass ratios of HAcI towards CNT from 0.07 to 14 are realized by adding appropriate amounts of nitrogen source. When no HAcI are used, palladium nanoparticles have a mean size of 2.33 nm with a standard deviation of 0.67 nm, slightly smaller than its counterpart 2Pd@CNT-DP catalysts. With the introduction of 21 mg of HAcI, both the mean size and distribution are nearly halved, resulting in quite a percentage of palladium clusters below 1 nm as shown in Figure 5.3.4 (b1) and (b2). When the nitrogen source is further increased to 105 mg, slightly bigger mean size and similar size distribution are obtained, suggesting that more HAcI can facilitate the growth of Pd nanoparticles. However, a surprising dramatic change in mean size is realized when 525 mg nitrogen sources are added, with almost 33.1% increase compared to only 20.9% when 105 mg are added. Moreover, size distributions are much broader too. Different catalytic activities are expected accompanying the surprising change in electronic structures of carbon nanotubes. With the further increase of HAcI, gradual change in mean size with a similar distribution can be maintained. Therefore, it can be seen that HAcI has a profound effect on the chemical properties of carbon nanotubes. Even very small amounts of it can change the interaction of Pd ions and CNT, reflected by the mean size and size distribution in Figure 5.3.4 (b1) and (b2). With the increase of HAcI, gradual changes in size can be realized. However, with appropriate amounts of nitrogen sources, in our case, 525 mg HAcI, dramatic modifications of CNT can also be achieved. The resulting differences in modification degree between various nitrogen-doped carbon nanotubes might be attributed to different amounts of total nitrogen dopants and different ratios of various nitrogen types. Such changes in CNT structures are expected to result in different catalytic activities for benzyl alcohol oxidation.

Figure 5.3.4 TEM graphs and Pd particle size distribution of (a1, a2) 2Pd@CNT; (b1, b2) 2Pd@CNT-HACl-1; (c1, c2) 2Pd@CNT-HACl-2; (d1, d2) 2Pd@CNT-HACl-3; (e1, e2) 2Pd@CNT-HACl-4; (f1, f2) 2Pd@CNT-HACl-5; (g1, g2) 2Pd@CNT-HACl-6.

The as-prepared catalysts are employed to benzyl alcohol oxidation reactions and the catalytic results are shown in Table 5.3.2. It can be seen all the catalysts based on nitrogen-doped supports have both higher conversion and higher selectivity towards benzaldehyde compared to that supported on pristine carbon nanotubes, confirming that palladium nanoparticles supported on nitrogen-doped carbon nanotubes indeed have better performance towards alcohol oxidation. For 2Pd@CNT-HACl-2 and 2Pd@CNT-HACl-3 catalysts particularly, more than twofold enhancement in benzyl alcohol conversion are obtained compared. However, initially, when small amounts of hydroxylamine chloride are added, slightly decreases in benzaldehyde selectivity are observed. It might due to the fact that defects derived from nitrogen doping can also promote the disproportionation route at the same time. With the increase of the amounts of nitrogen source added, better selectivity towards aldehyde is observed. This may be

attributed to the increase of base sites introduced by pyridinic nitrogen, which promotes the activation of O-H bonds during the oxidation step. More attention should be paid to 2.0Pd@CNT-HACl-5 catalysts, although only 1.76 times more benzyl alcohol conversion is obtained, 100% selectivity towards benzaldehyde can greatly simplify the after-reaction separation procedure. When more nitrogen source added, slightly decrease in selectivity towards aldehyde is observed with almost the same conversion efficiency. Therefore, 2.0Pd@CNT-HACl-5 has the best performance, with fully inhibition of the disproportion route and moderate conversion efficiency.

Table 5.3.2 Catalytic results of benzyl alcohol oxidation over palladium catalysts supported on CNT and a series of CNT-HACl by Absorption-Reduction Method.

Catalysts	Pd ^b (wt.%)	Conversion (%)	Selectivity (%)	
			Benzaldehyde	Toluene
2.0Pd@CNT	1.53	26.7	89.1	10.9
2.0Pd@CNT-HACl-1	1.84	49.5	82.6	17.4
2.0Pd@CNT-HACl-2	2.43	62.1	81.3	18.7
2.0Pd@CNT-HACl-3	2.17	65.2	89.1	10.9
2.0Pd@CNT-HACl-4	1.97	52.8	89.7	10.3
2.0Pd@CNT-HACl-5	1.97	47.2	100	0
2.0Pd@CNT-HACl-6	1.89	50.8	97.7	2.3

^a Reaction conditions: benzyl alcohol, 50 mmol; O₂, 20 mL min⁻¹; time, 3 h; temperature, 160 °C.

^b Metal content was obtained by ICP.

Figure 5.3.4 Effects of HAcI/CNT weight ratio on the selective oxidation of benzyl alcohol over palladium catalysts prepared by Absorption-Reduction Method.

Similar to many other noble metal-based catalysts, the particle sizes have a significant influence on the catalytic properties. As illustrated above, the size of Pd nanoparticles can be tuned by introduction of appropriate amounts of HAcI into the hydrothermal reaction system during nitrogen-doped carbon nanotubes preparation step. Therefore, the size effect can be investigated. Figure 5.3.5 shows the effects of HAcI/CNT weight ratio on Pd mean size and benzyl alcohol conversion over palladium catalysts prepared by Absorption-Reduction Method. It can be seen, the conversion of benzyl alcohol have exactly the same trend as mean size when increasing amounts of

nitrogen sources are charged, suggesting Pd nanoparticles with proper sizes are essential to obtain high conversion.

Figure 5.3.5 Effects of HAcI/CNT weight ratio on Pd mean size and benzyl alcohol conversion over palladium catalysts prepared by Absorption-Reduction Method.

Summary

A series of nitrogen-doped carbon nanotubes were successfully prepared using commercial available carbon nanotubes under a mild hydrothermal reaction system. Different kinds of nitrogen sources, including hydrazine hydrate coupled with ammonia, urea, hexamethylenetetramine, dicyandiamide, hydroxylamine chloride, are employed to modify the interesting tubular structure. It was demonstrated that different nitrogen sources can change the chemical and electronic properties of pristine carbon nanotubes with different extents. Palladium ions have a greater tendency to absorb on the modified

CNTs due to the existence of various types of nitrogen atoms, resulting much higher activity and higher selectivity towards aldehyde compared to its unmodified counterparts. To better understand the evolution of nitrogen doping, nitrogen-doped carbon nanotubes prepared with increased weight ratios of hydroxylamine chloride towards carbon nanotubes are prepared. All the palladium nanoparticles supported on modified carbon nanotubes have a smaller mean size and narrower distribution compared to unmodified ones. Even quite a small amounts of HAcI can decrease both of them by half. With the increase of HAcI, gradually bigger particles are obtained while the distribution can be maintained. When appropriate amounts of nitrogen sources are used, dramatic changes resulting abnormally larger particles are achieved. Such changes can also be reflected by the activity towards benzyl alcohol oxidation. Changes in benzyl alcohol conversion have exactly the same pattern as that of the mean particle size, with almost 2.5 times enhancement for 2Pd@CNT-HAcI-3. Different from the trend in conversion, monotonically increase in benzaldehyde selectivity is observed until 100% is realized over 2Pd@CNT-HAcI-5 catalysts. These results suggest gradually changes in carbon nanotubes can be realized by choosing appropriate type of nitrogen source and tuning reaction conditions through a simple and easy hydrothermal reaction, and the resulting carbon nanotubes are promising supporting materials for other oxidation reactions.

List of abbreviations

CNTs	Multi-Walled Carbon Nanotubes
ICP	Inductively coupled plasma
TEM	Transmission Electron Microscopy
XRD	X-Rays Diffraction
HACl	Hydroxylamine Chloride

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Chapter 6 Palladium Catalysts Supported on Zeolites for Selective Oxidation of Ethanol

In the global attempt to reduce carbon footprint, the chemical and petrochemical industry face the problem to replace the currently used fossil feedstocks with renewable resources. A viable alternative, gaining acceptance in recent years, is biomass-based alcohols, especially bio-ethanol. Bio-ethanol is a renewable energy source that can be easily produced from many biomass sources, including energy plants, grains, and waste materials of the agricultural and forestry industries and even from the organic fraction of municipal solid wastes. It is widely available, easy to store and transport and safe to handle.

Ethanol selective oxidation produces a variety of oxide products including acetaldehyde, acetal, acetone, acetic acid, ethylene oxide, diethyl ether and ethyl acetate, many of which are of paramount importance in chemical industry. Transition metal oxides, noble metal-based materials, zeolites, octahedral molecular sieves have been widely studied in ethanol selective oxidation reactions. For transition metals, V and Mo have been reported as highly active catalysts in ethanol oxidation with the primary product being acetaldehyde [1]. Ni [2], Ni-Fe [3] are also used as catalysts for partial oxidation of ethanol to hydrogen.

For noble metals, Au is the most extensively investigated catalyst for ethanol oxidation [4, 5]. In aqueous media, the product selectivity over Au catalyst is sensitive to the ethanol concentration: at low ethanol concentrations, the primary product is acetic acid; when the ethanol concentration is greater than 60 wt%, the product is then mainly ethyl acetate [5, 6]. Gold catalyst can also oxidize ethanol into other products, too.

Recently, the one-step production of ethylene oxide has been reported over Li^+ doped $\text{Au}/\text{Al}_2\text{O}_3$ [7], $\text{Ag}/\text{Al}_2\text{O}_3$ and $\text{Cu}/\text{Al}_2\text{O}_3$ [8]. In addition to gold catalyst, platinum was also extensively studied for ethanol selective oxidation. For example, Marin investigated oxidative dehydrogenation of aqueous ethanol into acetaldehyde and acetic acid on a carbon supported platinum catalysts [9]. Potassium- and sodium-promoted $\text{Pt}/\text{Al}_2\text{O}_3$ has been employed for the selective oxidation of ethanol to ethyl acetate. Nonetheless, ethyl acetate yield was poor along with other products such as diethyl ether, acetaldehyde, ethylene and carbon dioxide. Palladium catalysts were also attempted for ethyl acetate and acetic acid synthesis from ethanol oxidative dehydration [10]. However, the ethyl acetate selectivity of 70% is not economically satisfactory due to the high cost for product separation.

During oxidation reactions, noble metallic catalyst nanoparticles' sizes, their size distributions and the nature of support materials play important roles in influencing the catalytic activity for the reactions, and have therefore been studied extensively in recent years.

Using various techniques, many researchers have successfully proposed the mechanism for the reactions involved in ethanol selective oxidation. Over the metal surfaces, ethanol firstly undergoes O-H bond cleavage followed by selective β -C bond activation to form acetaldehyde [11]. Ethyl acetate formation originated from ethanol selective oxidation is generally accepted following the self-coupling mechanism. The selectivity of cross-coupling of alcohols depends on the anticipated tendency for the ethoxy groups to undergo β -hydrogen elimination, e.g., only methyl acetate was observed for methanol and ethanol cross-coupling [12], implying that the energy barrier

of β -hydrogen elimination of ethanol is remarkably lower than that of methanol. Therefore, self-coupling or cross-coupling of alcohols can be promoted if β -hydrogen elimination can be appropriately reinforced.

Zeolites, typically defined as hydrated, crystalline tectoaluminosilicates that are constructed from TO_4 tetrahedra, have been comprehensively used in oil processing, ion-exchange, guest-storage, hydrocarbon conversion, molecular recognition/sensing, size/shape selective heterogeneous catalysis, gas processes due to their unique physical and chemical properties since Barrer and coworkers successfully prepared the first synthetic zeolites in 1940s [13].

Underpinning all these applications are the well-defined pore structure, high thermostability and remarkable acidic properties of zeolites. Well-defined pore structure, apertures and cavities of approximately the size of organic molecules, exerts a steric influence on the reaction, controlling the access of reactants and products. The high thermostability of zeolites is another characteristic, which renders them particularly attractive for processes requiring repetitive regeneration steps at high temperatures. The choice of zeolite catalysts is also firmly due to their remarkable acidic properties. Indeed the density and strength of their acid sites can be varied on a large scale and can be adjusted to the desired catalytic reactions.

In bifunctional catalyst, a strong interaction between the acid site and metal particle has recently been investigated by experimental method [14, 15] and theoretical method, such as density functional theory [15], ONIOM (our-own-N-layered integrated molecular orbital and molecular mechanics) approach [16]. All of them had proved that reverse hydrogen spillover existed by a favorably thermodynamic process between metal

particles and zeolite provides a possibility for preparing catalysts with unique properties. In these bifunctional catalysts, M_mH_n was formed on the support surface and metal atom was riveted to oxygen atom on zeolite. The strong effect and specific M_mH_n species should make the bifunctional material possess an excellent stability and special selectivity oxidative activity.

Recently, the reverse hydrogen spillover energy (E_{rs}) for different metals on the same zeolite [17] or single metal on different supports [18] were investigated by theoretical method, the sequence of E_{rs} per transferred proton for $12M_6$ clusters supported in isolated zeolite fragments for the different metal almost is $Ir > Pt > Pd > Ag > Au$ [19]. So catalysts loaded with different metal nanoparticles should present different oxidative activity. Applied with these materials, ethanol as an active chemical resource can be oxidized to multitudinous products in chemical industrial.

In our group, supported Pd has been proved as efficient catalysts for selective oxidation of benzyl alcohol, showing remarkably high selectivity towards to benzaldehyde. Different supports significantly affected Pd activity and selectivity. The lower surface acidity surrounding the Pd nanoparticles improved the catalytic activity in benzyl alcohol dehydrogenation. A redox support such as $MnCeO_x$ mixed oxide effectively enhanced the stabilization of Pd nanoparticles along with the improved oxygen activation [20].

Herein, we investigated the gas-phase aerobic oxidation of ethanol to ethyl acetate through acetaldehyde intermediate (self-coupling mechanism) over zeolite supported Pd metallic nanoparticles. The influence of interaction between zeolite acidic site and oxidative center of Pd on the selectivity and consequently product distribution is also

studied. To further investigate and verify the effect of reverse hydrogen spillover on the unique catalytic activity and selectivity of Pd/HY catalyst in the aerobic oxidation of ethanol for ethyl acetate production, control experiments such as reactions under different temperatures, the reactions over different metals and different zeolite materials were carried out.

6.1 Preparation and characterization of Pd/HY bifunctional catalysts

Figure 6.1 TEM and XRD for 2Pd/HY before and after catalytic reaction.

1Pd/HY, 2Pd/HY, 2PdO/HY, 1Pt/HY, 2Au/HY, 15Ag/HY, 2Pd/ZSM5, 2Pd/H β and 2Pd/MOR, where 1, 2 and 15 denote weight percent of metal loadings, were prepared

by a deposition-precipitation method described in 3.2.7.

The Pd nanoparticle size and size distribution of 2Pd/HY before and after 73 hours reaction were examined by TEM measurement and the TEM images are illustrated in Figure 6.1. For fresh 2Pd/HY catalyst, spherical shape Pd nanoparticles with a narrow size distribution are uniformly dispersed on HY; the average particle size is measured at 5.7 ± 1.6 nm. HRTEM image of fresh 2Pd/HY sample shows some tiny Pd particles confined in the channels of HY zeolite. Powder X-ray diffraction shows the typical HY zeolite diffractions for fresh 2Pd/HY sample and no peaks originated from Pd diffraction can be clearly resolved. Larger Pd nanoparticles are observed over the spent catalyst after 73 hours reaction compared to fresh 2Pd/HY, and average particle size increases to 7.9 ± 2.3 nm. HRTEM image further confirms the existence of large Pd nanoparticles after the stability test. XRD characterization of spent 2Pd/HY catalyst shows enhanced peak intensity of the diffraction of HY support due to small amounts of coke deposition.

Analysis on weight loss (TGA) was carried out to further confirm the surface species for 2Pd/HY and the results are shown in Figure 6.2. Characterization of coke formation shows that only 0.04 wt.% of carbonaceous species is formed over 2Pd/HY after 73 hours reaction, suggesting Pd nanoparticles are effective in suppressing the coke deposition in ethanol selective oxidation. Nonetheless, a small amount of coke deposited on the catalyst may enhance the stability due to the suppressed Pd nanoparticle agglomeration. In addition, the carbonaceous deposits may selectively deactivate certain specific type of active sites, which is crucial in determining its influence on reaction selectivity.

Figure 6.2 TGA for 2Pd/HY before and after reaction.

6.2 Catalytic performance of Pd/HY bifunctional catalysts

Table 6.1 Catalytic performance of bi-functional Pd/zeolite catalysts for ethanol partial oxidative reaction, atmospheric pressure.

Samples	Reaction temperature (°C)	Ethanol conversion (%)	Selectivity (%)					
			Total of dehydration	Ethylene/di-ether	Selective oxidation	Acetaldehyde/EA	Acetic acid	CO ₂
HY	150	80.6	33.7	1.1/32.6	63.6	57.6/6.0	0	0
	250	100	100	100/0	0	0/0	0	0
1Pd/HY	150	93.2	8.4	2.7/5.7	87.8	76.8/11.0	3.7	0
	250	90.1	32.7	28.6/4.1	16.7	6.2/10.5	50.3	0.2
2Pd/HY	80	79.2	1.2	1.2/0	98.8	27.1/71.7	0	0
	150	84.6	4.6	3.5/1.1	93.9	2.1/91.8	1.5	0
	250	93.5	28.8	28.8/0	6.3	0/6.3	52.8	12.1
2PdO/HY	150	54.9	0	0/0	100	89.0/11.0	0	0
	250	46.9	21.3	13.4/7.9	78.7	61.5/17.2	0	0

^a Reaction conditions: catalyst, 100 mg (the amount of Pd is 2 wt.% of catalyst, 2mg); The feed, a mixture of ethanol and O₂ (1:2 mol) in He with the flow rates of 0.016, 3 and 22.4 ml/min for ethanol, O₂ and He, respectively.; temperature, 80 °C, 150 °C, 250°C; time, 0.5hr.

The catalytic activities of these as-prepared catalysts were explored by selective oxidation of ethanol. As shown in Table 6.1, all the catalysts show superior activities, and the ethanol conversion is constantly higher than 80%. The products can be divided into three categories: dehydration, partial oxidation and deep oxidation products. Dehydration products such as diethyl ether and alkene have been reported on acidic zeolites and TiO₂-impregnated silicalite-I dehydrates at high temperatures [21]. In this study, HY zeolite in the absence of any metal shows reasonably high selectivity towards acetaldehyde (57.6%) at low temperature. Remarkably high dehydration selectivity due to its strong acidity is observed at high temperature. Moreover, high temperature favors the intra-molecular dehydration, showing 100% selectivity towards ethylene. The dehydration selectivity decreases from 33.7 % to 8.4 % at 150 °C reaction temperature when the Pd loading is increased from 0 to 1 wt%, indicating that Pd as the oxidation sites can effectively suppress the acid reactions. Acetaldehyde is the primary partial oxidative product on both HY and 1 wt. % Pd/HY catalysts. When further increases the Pd loading, remarkably high partial oxidation selectivity (93.9%) is obtained. Surprisingly, ethyl acetate is the main product, showing the selectivity of 91.8%. For the aerobic oxidation of alcohol over supported Pd nanoparticles, Christopher et al. reported that highly dispersed palladium oxide nanoparticles were the catalytically active species to transform alcohols to their corresponding aldehydes [22]. In this study,

PdO/HY was also prepared for control purposes, and its catalytic performance in ethanol oxidation is also listed in Table 6.1. PdO/HY shows the poor ethanol conversion but remarkably high selectivity towards acetaldehyde.

On the other hand, Liu et al. reported that the adsorbed O species indeed played the vital role in controlling the product selectivity in the ethanol oxidation on Au (111) surfaces. At a relatively low surface O coverage, the predominant product of ethanol oxidation is ethyl acetate, no significant deep oxidation product such as acetic acid or complete oxidation product (CO_2) evolution occurred under these conditions, showing nearly 100% selectivity for esterification [23]. When the initial O concentration increased to 0.2 ML, remarkable oxidation to acetic acid, ketene and CO_2 at the expense of formed ester is found. The oxygen concentration (in terms of ethanol: O_2 ratio) effect was studied at 150 °C in this study and the results are depicted in Figure 10. 2Pd/HY is selected as the catalyst and the ethanol conversion and the selectivity towards ethyl acetate, acetaldehyde, ethylene and acetic acid are plotted against reaction time on stream. Initially, the ethanol and oxygen mixture at a 1:1 molar ratio was attempted and 21% acetaldehyde selectivity and 70 % ethyl acetate selectivity were obtained. Ethanol conversion gradually increases along the time on reaction stream with the increased selectivity towards ethyl acetate at the expense of formed acetaldehyde, implying that aerobic oxidation of ethanol to ethyl acetate may go through the self-coupling mechanism in which acetaldehyde is the intermediate. The ethyl acetate selectivity abruptly decreases and a substantial amount of acetic acid is produced when the reaction proceeds over 6 hours, indicating that deep oxidation of ethyl acetate overrides the ethanol self-coupling reaction in the presence of excess amounts of oxygen. When the

flow was switched to 2:1 of ethanol: O₂ molar ratio reaction stream ($2\text{C}_2\text{H}_6\text{O} + \text{O}_2 = \text{C}_4\text{H}_8\text{O}_2 (\text{ethyl acetate}) + 2\text{H}_2\text{O}$), acetic acid gradually disappears and ethyl acetate selectivity increases sharply back to the original value (~90%).

Figure 6.3 Ethanol conversion and distribution of products.

Nonetheless, the ever-increasing attention towards the economical and environmental sustainability of organic chemical production is thus prompting the scientific community to develop solid catalysts that are less prone to deactivation. Deactivation of zeolite, especially HY type, always occurs with a concomitant mass increase due to coke deposition. We tested the catalyst stability over a long reaction time on stream and the results are shown in Figure 6.3. The activity as represented by ethanol conversion and selectivity towards ethyl acetate are essentially stable after 73 hours. This is in accordance with the stable property of bifunctional catalyst (Pd on zeolite).

6.3 Summary of Pd/HY bifunctional catalysts

A series of Pd/HY bifunctional catalysts have been successfully prepared with deposition-precipitation method. The catalytic activity of these as-produced catalysts has been explored with a solvent free selective oxidation of ethyl alcohol using molecular oxygen, while the properties of these catalysts were examined through TEM, XRD, FTIR, TGA and stability test. Characterization results proved that Pd nanoparticles are effective in suppressing the coke deposition in ethanol selective oxidation and a small amount of coke deposited on the catalyst may enhance the stability due to the suppressed Pd nanoparticle agglomeration. In conclusion, Pd/HY bifunctional catalyst was demonstrated as a unique catalyst for ethanol oxidation to afford high yield one-step synthesis of acetaldehyde and ethyl acetate, especially the ethyl acetate formation, 91.8% of ethyl acetate selectivity at 150 °C and 84.2 % of ethyl acetate yield were achieved over 2Pd/HY catalyst at 210 °C. The product selectivity can be readily tuned by changing the reaction condition parameters. The reverse hydrogen spillover effect was identified to take place between Pd nanoparticles and zeolite support, which can well balance the oxidative activity and acidity at an appropriate reaction temperature. Pd/HY catalyst was remarkably stable at low reaction temperature during the reaction and only a small amount of coke was deposited.

6.4 In-depth study of catalytic performance of bifunctional catalysts

To further investigate and verify the effect of reverse hydrogen spillover on the unique catalytic activity and selectivity of Pd/HY catalyst in the aerobic oxidation of ethanol for ethyl acetate production, control experiments such as reactions under different temperatures, the reactions over different metals and different zeolite materials

were carried out. On a zeolite supported noble metal nanoparticle bi-functional catalyst, hydrogen reversely spillover from zeolite to metal clusters by single proton transfer is an exothermal step and favors low temperature. Under the high reaction temperature (250 °C), acid-catalyzed reaction is significantly improved due to the proton transferring back from metal nanoparticles to zeolite surfaces. In addition, deep oxidation to form acetic acid and CO₂ is also enhanced because of the adsorbed oxygen species under the “lean” proton condition on Pd surfaces.

Table 6.2 Catalytic performance of different metal-based bi-functional catalysts for ethanol partial oxidative reaction, atmospheric pressure.

Samples	Reaction temperature (°C)	Ethanol conversion (%)	Selectivity (%)					
			Total of dehydration	Ethylene/ di-ether	Selective oxidation	Acetaldehyde/ EA	Acetic acid	CO ₂
1Pt/HY	150	97.5	0	0/0	3.5	2.1/1.4	96.4	0.1
	250	100	0	0/0	0	0/0	93.3	6.7
1Au/HY	150	98.0	78.8	0.9/77.9	20.2	17.4/2.8	1.1	0
	250	94.0	46.5	39.8/6.7	50.8	21.5/29.3	2.8	0
2Au/HY	150	88.0	74.5	0.7/73.8	25.5	19.7/5.8	0	0
	250	94.0	36.5	34.7/1.8	60.5	8.6/51.9	3.1	0
15Ag/HY	150	60.9	3.8	0/3.8	94.7	84.6/10.1	3.2	0
	250	65.0	31.4	11.6/19.8	63.7	45.0/18.7	3.7	0

Reaction conditions: catalyst, 100 mg; The feed, a mixture of ethanol and O₂ (1:2 mol)

in He with the flow rates of 0.016, 3 and 22.4 ml/min for ethanol, O₂ and He, respectively.; temperature, 150 °C, 250°C; time, 0.5hr.

Different metals on zeolite will significantly affect the synergetic interaction between metal nanoparticles and zeolite substrate [24]. Table 6.2 shows the catalytic performance of different metal-based bi-functional catalysts for ethanol partial oxidative reaction at atmospheric pressure. Over the Pt supported on HY catalyst

(Pt/HY), there are no dehydration products and the main products come from deep oxidation, suggesting the weak acidity due to the strong reverse hydrogen spillover effect of the catalysts and highly oxidative activity of Pt. Reaction temperature shows dramatic effect on the gold catalysts. The dehydration pathways are significantly suppressed when increasing the reaction temperature from 150 to 250 °C. Moreover, deep oxidation products are not significant due to the weak capability of gold in oxidation of ethanol. Over the Au/HY shows weak reverse hydrogen spillover effect. Nonetheless, the yields of partial oxidative products over Au/HY are less. Au/HY makes more di-ether (77.9% selectivity) than HY at 150 °C, indicating that the effect of Au loading is more for improving intermolecular dehydration of ethanol than partial oxidation. Silver as an effective oxidative catalyst for ethylene oxide formation was also prepared and tested in the ethanol oxidative dehydration. The product distribution is mainly concentrated on the partial oxidative products, especially acetaldehyde; no ethylene oxide is seen. Ethylene oxide requires γ -hydrogen activation while acetaldehyde formation undergoes β -hydrogen activation. The reverse hydrogen spillover effect is an exothermic process, higher temperature makes less reverse hydrogen spillover and more acidity on sample, so the dehydration products increased when reaction temperature increased, like dehydration production increased on 15Ag/HY sample. Ethyl acetate selectivity increased and acetaldehyde decreased with

temperature increased due to high temperature must make more adsorbed ethanol to produce ethyl acetate.

Figure 6.4 IR spectra of pyridine adsorption at different temperature for 2Pd/HY, 2Pd/Hβ, 2Pd/MOR and 2Pd/ZSM5, dotted and solid lines desorpt pyridine at 150 °C, and 50 °C, respectively.

In this study, other types of zeolite such as MOR, H-beta and ZSM5 were also examined as the support. The reverse hydrogen spillover effect should play the role to different extent because different zeolite possesses different acidity. Figure 6.4 exhibits the IR spectra of pyridine adsorption at different temperature for 2Pd/HY, 2Pd/Hβ, 2Pd/MOR and 2Pd/ZSM5 samples. The three major bands at 1497, 1544, and 1630 cm⁻¹ observed for Pt/zeolites sample can be assigned to pyridine coordinated to protons.

But only that at 1544 cm^{-1} is typical for pyridinium ions, be related to Brønsted acid sites [25]. Nevertheless, minor band at $1442\text{--}1456\text{ cm}^{-1}$ could be detected, which is caused by the interaction of pyridine with Lewis acid sites [26]. In the spectra obtained on all kinds of samples, Lewis acid intensity sequence is $2\text{Pd}/\text{MOR} > 2\text{Pd}/\text{H}\beta \approx 2\text{Pd}/\text{ZSM5} > 2\text{Pd}/\text{HY}$. The ring stretching modes of hydrogen-bonded and physically adsorbed pyridine are clearly observed at 1439 and 1598 cm^{-1} . The observed decrease in IR band intensity is due to the desorption of pyridine. It decreases slowly from 323 K to 423 K .

Figure 6.5 Effect of reaction temperature on ethyl acetate yield over Pd supported on different zeolites samples.

The ethyl acetate yield is plotted against reaction temperature for different zeolite supported Pd catalysts and the results are shown in Figure 6.5. The yield of ethyl acetate show the same trend with reaction temperature over different zeolite supports. Highest yield about 80% can be obtained over all the catalyst at an appropriate reaction temperature except for H-beta catalyst. The largest ethyl acetate yield of 84.2% is obtained on 2Pd/HY sample at 210 °C reaction temperature. The ethyl acetate yields decrease with reaction temperature due to the suppressed reverse spillover hydrogen at high temperature for all the catalysts. Interestingly, the most suitable reaction temperature (T_{sample}) is different on different samples for ethyl acetate production, The order for the most suitable reaction temperature: $T_{2\text{Pd/MOR}} < T_{2\text{Pd/ZSM5}} \approx T_{2\text{Pd/H}\beta} < T_{2\text{Pd/HY}}$, implying that the support acidity indeed improves the ethyl acetate production at low reaction temperature because strong acidity improves the dehydration and partial oxidation steps to produce ethyl acetate.

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Chapter 7 Conclusions and Future Perspectives

7.1 Conclusions

For selective oxidation reactions of benzyl as well as ethyl alcohol based on noble-metal heterogeneous catalyst, supporting materials, reaction temperature as well as other reaction conditions have a profound influence in the activity as well as the selectivity. In this study, palladium catalysts deposited on a widely used metal oxide with different morphologies, namely titanium dioxide nanoparticles and nanowires, have been employed to investigate the effects of reaction temperature, catalysts/substrate molar ratio, reaction duration and oxygen flow rate. For all the catalysts, benzaldehyde is the major product, with toluene and water the only byproducts. No further oxidative compounds are obtained, suggesting the excellent controllability of as-prepared catalysts in inhibiting deeper oxidation reaction. It is found that water is the main reason for catalysts deactivation and removal of the toluene produced at early stages in time might be able to fully inhibit the disproportion route, resulting in almost 100% selectivity towards aldehyde. Although catalysts based on titanium dioxide nanoparticles have better activity compared to their nanowire counterparts, much lower aldehyde selectivity is its main disadvantage. With 100% selective towards benzaldehyde and excellent stability, further modification of palladium catalysts supported on titanium dioxide nanowire have the potential to be used in large-scale synthesis of benzaldehyde through benzyl alcohol oxidation. Different preparation methods also have a great impact on the catalytic performance of palladium catalysts. Two common methods, urea-assisted deposition-precipitation and incipient wetness impregnation methods are commonly used to deposit noble metal ions

on various supporting materials. It is found that catalysts prepared by the impregnation method have larger metal loadings with a broader size distribution than those prepared by a deposition-precipitation method, resulting in much higher activity with lower selectivity towards benzaldehyde. However, the palladium loadings are quite low even with high concentration of palladium precursors due to the large repulsion force between the hydroxyl group-rich titanium dioxide nanoparticles and palladium complex at elevated pH. For the effects of supporting materials, it can be seen catalysts based on P25 nanoparticles have better activity than their titanium dioxide nanowire counterparts with same metal loadings, which can be attributed to better crystallinity and less defects of nanowire supports. Also, the metal loadings have less influence on the catalysts prepared by impregnation method, suggesting 0.5 wt.% loadings is enough for them to be saturated in the present catalytic system. A further loading on TNW using a DP method might be able to increase the activity further more.

The acid-base properties of supporting materials can also play a vital rule in benzyl alcohol oxidation. Basic site can effectively decrease the nanoparticle sizes and narrow the size distribution, which will provide more active sites for catalytic reaction. Furthermore, base sites are often participate in the benzyl alcohol oxidation reaction as promoters. Therefore, a series of nitrogen-doped carbon nanotubes were successfully prepared using commercial available carbon nanotubes under a mild hydrothermal reaction system to investigate the acid-base effects of these supports in benzyl alcohol oxidation. Different kinds of nitrogen sources, including hydrazine hydrate coupled with ammonia, urea, hexamethylenetetramine, dicyandiamide, hydroxylamine chloride, are employed to modify the interesting tubular structure. It was demonstrated that

different nitrogen sources can change the chemical and electronic properties of pristine carbon nanotubes with different extents. Palladium ions have a greater tendency to absorb on the modified CNTs due to the existence of various types of nitrogen atoms, resulting much higher activity and higher selectivity towards aldehyde compared to its unmodified counterparts. To better understand the evolution of nitrogen doping, nitrogen-doped carbon nanotubes prepared with increased weight ratios of hydroxylamine chloride towards carbon nanotubes are prepared. All the palladium nanoparticles supported on modified carbon nanotubes have a smaller mean size and narrower distribution compared to unmodified ones. Even quite a small amounts of HAcI can decrease both of them by half. With the increase of HAcI, gradually bigger particles are obtained while the distribution can be maintained. When appropriate amounts of nitrogen sources are used, dramatic changes resulting abnormally larger particles are achieved. Such changes can also be reflected by the activity towards benzyl alcohol oxidation. Changes in benzyl alcohol conversion have exactly the same pattern as that of the mean particle size, with almost 2.5 times enhancement for 2Pd@CNT-HAcI-3. Different from the trend in conversion, monotonically increase in benzaldehyde selectivity is observed until 100% is realized over 2Pd@CNT-HAcI-5 catalysts. These results suggest gradually changes in carbon nanotubes can be realized by choosing appropriate type of nitrogen source and tuning reaction conditions through a simple and easy hydrothermal reaction, and the resulting carbon nanotubes are promising supporting materials for other oxidation reactions.

Ethanol selective oxidation produces a variety of oxide products including acetaldehyde, acetal, acetone, acetic acid, ethylene oxide, diethyl ether and ethyl acetate,

many of which are of paramount importance in chemical industry. A series of Pd/HY bifunctional catalysts have been successfully prepared with deposition-precipitation method to investigate their catalytic activity in solvent-free selective oxidation of ethyl alcohol. Characterization results proved that Pd nanoparticles are effective in suppressing the coke deposition in ethanol selective oxidation and a small amount of coke deposited on the catalyst may enhance the stability due to the suppressed Pd nanoparticle agglomeration. Pd/HY bi-functional catalyst was demonstrated as a unique catalyst for ethanol oxidation to afford high yield one-step synthesis of acetaldehyde and ethyl acetate, especially the ethyl acetate formation, 91.8% of ethyl acetate selectivity at 150 °C and 84.2 % of ethyl acetate yield were achieved over 2Pd/HY catalyst at 210 °C. The product selectivity can be readily tuned by changing the reaction condition parameters. The reverse hydrogen spillover effect was identified to take place between Pd nanoparticles and zeolite support, which can well balance the oxidative activity and acidity at an appropriate reaction temperature. Pd/HY catalyst was remarkably stable at low reaction temperature during the reaction and only a small amount of coke was deposited. To further investigate and verify the effect of reverse hydrogen spillover on the unique catalytic activity and selectivity of Pd/HY catalyst in the aerobic oxidation of ethanol for ethyl acetate production, control experiments such as reactions under different temperatures, the reactions over different metals and different zeolite materials were carried out. On a zeolite supported noble metal nanoparticle bi-functional catalyst, hydrogen reversely spillover from zeolite to metal clusters by single proton transfer is an exothermal step and favors low temperature. Under the high reaction temperature (250 °C), acid-catalyzed reaction is significantly

improved due to the proton transferring back from metal nanoparticles to zeolite surfaces. In addition, deep oxidation to form acetic acid and CO_2 is also enhanced because of the adsorbed oxygen species under the “lean” proton condition on Pd surfaces.

Different metals on zeolite will significantly affect the synergetic interaction between metal nanoparticles and zeolite substrate. Over the Pt supported on HY catalyst (Pt/HY), there are no dehydration products and the main products come from deep oxidation, suggesting the weak acidity due to the strong reverse hydrogen spillover effect and highly oxidative activity of Pt. Reaction temperature shows dramatic effect on the gold catalysts. The dehydration pathways are significantly suppressed when increasing the reaction temperature from 150 to 250 °C. Moreover, deep oxidation products are not significant due to the weak capability of gold in oxidation of ethanol. Over the Au/HY shows weak reverse hydrogen spillover effect. Nonetheless, the yields of partial oxidative products over Au/HY are less. Au/HY makes more di-ether (77.9% selectivity) than HY at 150 °C, indicating that the effect of Au loading is more for improving intermolecular dehydration of ethanol than partial oxidation. Silver as an effective oxidative catalyst for ethylene oxide formation was also prepared and tested in the ethanol oxidative dehydration. The product distribution is mainly concentrated on the partial oxidative products, especially acetaldehyde; no ethylene oxide is seen. Ethylene oxide requires γ -hydrogen activation while acetaldehyde formation undergoes β -hydrogen activation. The reverse hydrogen spillover effect is an exothermic process, higher temperature makes less reverse hydrogen spillover and more acidity on sample, so the dehydration products increased when reaction temperature increased, like

dehydration production increased on 15Ag/HY sample. Ethyl acetate selectivity increased and acetaldehyde decreased with temperature increased due to high temperature must make more adsorbed ethanol to produce ethyl acetate.

7.2 Future Perspectives

Titanium dioxide nanowires with better crystallinity can be synthesized in large scale by a simple molten salt reflux method. Palladium catalysts supported on those nanowires have extraordinary selectivity towards benzaldehyde, with no byproducts for all reaction conditions investigated. However, due to high temperature employed in the preparation step of nanowires, most of the functional groups on the surface have been wiped off, resulting in much larger palladium particle sizes compared to those deposited on nanoparticles. A post-functionalization technique with amine group-rich compounds such as (3-aminopropyl)triethoxysilane might be able to tailor the surface properties of titanium dioxide nanowires and thus enhance its interaction with palladium ions, resulting in smaller particle sizes and more active sites for subsequent catalytic reactions. An alternative route is to incorporate nitrogen atoms into the lattice by a high temperature calcination procedure in ammonia atmosphere or much simpler hydrothermal method. The nitrogen-doped titanium dioxide are believed to have quite different electronic properties compared to pristine ones, and might be able to provide more anchoring points for palladium deposition.

Nitrogen doping is proved to have dramatic influence in the electronic properties of carbon nanotubes, resulting in much smaller palladium particle sizes and narrower size distributions. Various nitrogen sources have been studied, and they all can improve the catalytic activity of palladium nanoparticles in benzyl alcohol oxidation. However,

different reaction mechanisms might exist for different nitrogen sources, as illustrated by the different catalytic results for benzyl alcohol oxidation. Apart from the deeply investigated nitrogen source in this thesis, hydroxylamine chloride, the use of other types alone or a mixed compounds might be capable to modify the carbon nanotubes with different extents and thus have much more enhancement in decrease the palladium particle sizes. Another path is to prepare nitrogen-rich carbon nanotubes through a one-step procedure by pyrolysis of dicyandiamide in high temperatures. Those nitrogen-containing species are believed to have quite different electronic properties, which would influence the deposition of various noble metal ions for catalytic reactions.

Appendix

Journal Publications

- Jinlin Long, Shuchao Wang (co-first), Hongjin Chang, Baozhou Zhao, Botong Liu, Yangen Zhou, Wei, Wei, Xuxu Wang, Ling Huang and Wei Huang, Bi₂MoO₆ Nanobelts for Crystal Facet-Enhanced Photocatalysis, *Small*, 2014, 14, 2791-2795.
- Ping Yang, Shuchao Wang, Xue Teng, Wei, Wei, Vinayak P. Dravid and Ling Huang, Effect of Magnetic Nanoparticles on the Morphology of Polystyrene-b-Poly(methyl methacrylate) Diblock Copolymer Thin Film, *Journal of Physical Chemistry C*, 2012, 43, 23036-23040.
- Xue Teng, Yihan Zhu, Wei, Wei, Shuchao Wang, Jingfeng Huang, Rafik Naccache, Wenbo Hu, Alfred Iing Yoong Tok, Yu Han, Qichun Zhang, Quli Fan, Wei Huang, John A. Capobianco and Ling Huang, Lanthanide-Doped Na_xScF_{3+x} Nanocrystals: Crystal Structure Evolution and Multicolor Tuning, *Journal of the American Chemical Society*, 2012, 20, 8340-8343.
- Jinlin Long, Sibao Wang, Zhengxin Ding, Shuchao Wang, Yangen Zhou, Ling Huang and Xuxu Wang, Amine-functionalized zirconium metal-organic framework as efficient visible-light photocatalyst for aerobic organic transformations, *Chemical Communications*, 2012, 95, 11656-11658.
- Jinlin Long, Hongjin Chang, Quan Gu, Jie Xu, Lizhou Fan, Shuchao Wang, Yangen Zhou, Wei, Wei, Ling Huang, Xuxu Wang, Ping Liu, and Wei Huang, Gold-plasmon enhanced solar-to-hydrogen conversion on the {001} facets of anatase TiO₂ nanosheets, *Energy & Environmental Science*, 2014, 3, 973-977.

- Shuhcao Wang, Yihu Dai, Yanhui Yang, Palladium nanoparticles supported on titanium dioxide nanowires for solvent-free aerobic oxidation of benzyl alcohol, *Catalysis Today*, (in preparation).
- Shuhcao Wang, Yihu Dai, Yanhui Yang, Palladium nanoparticles supported on nitrogen-doped carbon nanotubes for benzyl alcohol oxidation, *Journal of Catalysis*, (in preparation).