Surface functionalization design of carbon materials based heterogeneous catalysis for selective oxidative transformations

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2015

Yan, Y. (2015). Surface functionalization design of carbon materials based heterogeneous catalysis for selective oxidative transformations. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/65469>

<https://doi.org/10.32657/10356/65469>

**Surface Functionalization Design of Carbon Materials Based
Heterogeneous Catalysis for Selective Oxidative
Transformations**

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A THESIS FOR
DOCTOR OF PHILOSOPHY DEGREE
SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING
NANYANG TECHNOLOGICAL UNIVERSITY
2015

Abstract

The processes of alcohols selectively oxidized to corresponding aldehydes or ketones play a vital role in either industry or laboratory because of the carbonyl versatility in organic synthesis. Owing to the recyclability, heterogeneous catalysts are superior to homogeneous catalysts under a wide range of reaction conditions. Besides catalytic activity, selectivity of a heterogeneous catalyst also plays a significant role especially in fine chemical industry. Selective oxidation of benzyl alcohol mainly forms benzaldehyde serving as flavor and precursor to valuable pharmaceuticals or plastic additives, while oxidation of glycerol generates chemicals including glyceric acid, a valuable intermediate, and dihydroxyacetone, an active ingredient in sunless tanning lotions. In this study, several sets of heterogeneous catalysts based on surface-functionalized carbon materials have been synthesized to catalyze the alcohol oxidation reactions and meanwhile the intrinsic mechanism of property-performance interactions are unraveled through a variety of characterizations. Both the Sm_2O_3 and 3-aminopropyl triethoxysilane functionalization of CNTs supported Pd catalysts displayed the high improvement in catalytic activity whereas the content of promoter had impact on Pd particle size, electrochemical surface area, and metal-support interactions which further influenced the benzyl alcohol conversion and selectivity toward benzyl aldehyde. New understandings of catalyst design specifically focused on the catalytic preparation strategies, physicochemical characteristics of active sites, surface chemistry and the specific metal-support interactions have been discussed in detail.

Recently, a “green” synthetic approach free of toxic reagents and organic solvents has been established to transform the readily prepared carbohydrate precursors to generate

carbon spheres by simply using hydrothermal autoclaves at the temperature varied from 160 °C to 180 °C. Alkaline carbon nano-spheres (CNSs) prepared by hydrothermal approach and post-functionalization with alkali solutions were employed as solid base catalysts in aldol condensation between benzaldehyde and acetaldehyde to form cinnamaldehyde. The decent negative charge and alkalinity of CNSs surface were controlled by the treatment concentration of alkali solutions, leading to high selectivity superior to aqueous NaOH as the traditional catalyst. Furthermore, CNSs with varying surface alkalinity can be adopted as proper supports for highly dispersed Pd nanoparticles with well-controlled size distribution. Those optimized alkaline CNSs supported Pd catalysts demonstrated enhanced reactivities in the solvent-free selective oxidation of benzyl alcohol and the aerobic oxidation of glycerol. In-depth characterizations of their structural and electronic properties by transmission electron microscope (TEM), field emission scanning electron microscope (FESEM), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were performed to elucidate the nature of the active sites and the mechanism. The effect of electron density, size of Pd nanoparticles as well as the surface alkalinity of supports on the catalytic performance has been unveiled.

Acknowledgements

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

I really appreciate the valuable instructions, discussion, advices and supports from Dr Yuanting Chen, Dr Yihu Dai, Dr Wenjin Yan and Dr. Zhen Guo. I also want to thank all the research group members who helped and encouraged me. They are Mr. Jun Zhao, Mr. Yong Yan, Mr. Shuchao Wang, Mr Jijiang Huang, Ms. Linlu Bai, Ms. Qian Zhang, Mr. Xiaoping Chen, Dr. Kaixin Li, Dr. Hong Chen, Dr. Chunmei Zhou and Mr. Amaniampong Prince Nana.

I have to show gratitude to my families, including my mother for her sincere understanding and backing.

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

Last but not least, I need to show my genuine gratitude to Professor Yanhui Yang, my Ph.D. supervisor, because he always provides most valuable suggestions; because he trusts me and permits me to do everything I want to with sufficient funding and professional conditions in lab.

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Chapter 1 Background and Philosophy

1.1 Background and the advantage of functionalized carbon materials for heterogeneous catalysis

The Swedish chemist Berzelius suggested a new force in 1835, catalytic force which was called catalysis, after reviewing a lot of early studies of chemical reactions [1]. This concept of catalysis was afterward consolidated by many other pioneer chemists including Davy, Thénard, Ostwald, Döbereiner, and Taylor [1, 2]. Currently, catalysts are well known for their role of dramatically accelerating the reaction rate without being consumed during reactions. Catalytic processes have been applied in various essential industries such as energy, environment, pharmaceutical, commodity, agriculture, electronics and so forth [3-5]. As a recognized benchmark in academia, the Chemistry Nobel Prizes have been awarded 13 years to honorees working in the field of catalytic chemistry by 2014. The early stage of catalyst is usually homogeneous catalysts which are in the same phase of reactants. In recent years, tremendous attention has been dedicated into developing recyclable and reusable heterogeneous catalysts for atom economic concerns to take the place of conventional stoichiometric procedures within homogeneous systems which consume expensive additives and give rise to liquid waste containing inorganic salts.

As high specific surface area materials with outstanding physical chemical properties, carbon materials, such as carbon nanotubes, graphite, activated carbon, carbon black and mesoporous carbon materials have attracted tremendous attention in a wide range of applications since they can be produced inexpensively from various low-priced precursors and are chemically stable under non-oxidative conditions. They possess low

density, high thermal conductivity, mechanical stability and fine electrical conductivity or semi-conductivity. They have been well applied to fields of catalysis, electrodes, batteries, sensing, sorption, energy storage and gas storage. In terms of heterogeneous catalysis, carbon materials can serve as either catalysts or catalyst support. Activated carbon catalysts have been used for fuel gas cleaning, the simultaneous SO_2/NO_x removal process [6-8], dehydrogenation of hydrocarbon [9-11], dehydration and dehydrogenation of alcohols [12-17]. Carbon materials supported catalysts are generally realized by impregnation [18, 19], precipitation [20], in-situ reduction in liquid phase [21] and so forth. The carbon supported ruthenium-based catalysts have been long used for ammonia synthesis process [22-25]. The carbon supported catalysts are used for hydrotreating reactions including the hydrodesulfurization and hydrodenitrogenation procedures [26-35]. Hydrogenation reactions are among the most important industrial applications of carbon supported catalysts. The relatively inert carbon surface is an essential advantage when carbon materials are used as support for hydrogenation catalysts, usually favoring the reducibility of active phase. Carbon supported catalysts have been extensively investigated for the hydrogenation of carbon oxides, i.e., CO or CO_2 , to generate methane and hydrocarbons, also known as Fischer–Tropsch process [36-44].

According to the requirement for specific application, surface of carbon materials are imposed with functionalization so as to fine-tune the bulk and surface properties and adjust the interactions with guest particles or molecules. The general approaches of surface functionalization include direct incorporation of heteroatoms, surface oxidation and activation, grafting with functional groups or polymers, halogenation, sulfonation and attachment of nanoparticles. The surface acid treatment was widely used to create

oxygen-containing groups such as ketone, phenol, lactone, carboxyl group, ether, acid anhydride, etc. These oxygen-containing groups can improve the hydrophilicity, can serve as anchoring sites for subsequent functionalization, can play a better role as mechanical reinforcements due to the more sufficient dispersion and enhanced interface interactions [45, 46]. The surface quinone and hydroquinone are redox active sites leading to larger capacitance of CNTs [47]. The direct doping with nitrogen atoms can provide additional electrons and thus improve the electronic transfer kinetics, conductivity and electrochemically active surface area of catalysts [48, 49]. Carbon materials functionalized with sulfonic acid groups have been used as environmentally friendly solid-acid catalysts for rearrangement, dehydration esterification, and condensation reactions [50, 51]. Surface fluorination is developed to promote the surface hydrophobicity of carbon materials via a variety of methods [52-54]. Surface bromination of carbon materials is a useful method to create anchoring groups on carbon surface for the subsequent substitution of a wide range of nucleophiles such as amines, anilines, alcohols, and thiols, etc [55, 56]. The broadest range of surface functional groups on carbon materials are possible by grafting approach usually based upon the presence of surface oxygen species in order to design the expected surface properties of carbon materials [57]. Besides organic functionalization of carbon surface, a wide range of methods have been developed to functionalize carbon materials with nanoparticles, mainly classified into: nanoparticle dispersion on carbon surface, physiochemical attachment, electrochemical deposition and electroless deposition [58]. These are critical methodologies in catalytic preparations.

1.2 Aims and outline of this dissertation

Considering the academic and industrial significance of heterogeneous catalytic process for alcohol selective oxidation, benzyl alcohol selective oxidation and stereoselective oxidation of glycerol are selected as target reactions for investigation in this Ph.D. study, intending to understand and design optimal heterogeneous catalysts for specific reactions. In the selective oxidation of benzyl alcohol, different surface functionalization approaches were employed to prepare modified CNTs supported or carbon nanosphere loading metallic catalysts via ion adsorption reduction method. The surface functionalization techniques include surface acid oxidation, grafting with organosilanes groups, attachment of rare earth oxides and surface alkali treatment. The catalysts were characterized using a series of characterization techniques, e.g., X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), field emission scanning electron microscope (FESEM) and X-ray diffraction (XRD), RAMAN spectra, Fourier transmission infrared spectroscopy (FTIR), inductively coupled plasma (ICP) and zeta potential. Additionally, the electrochemical property of catalytic support and catalysts are shed light on by using cyclic voltammetry (CV) and CO stripping voltammograms. These results will be presented in detail by Chapter 4.

Numerous effective heterogeneous catalysts usually constitute of metal nanoparticles supported on substrate materials have been developed for alcohol oxidation. Abundant substrate materials have been utilized as the catalytic supports, among all of which CNTs attracted a lot of curiosity due to the high electrical conductivity, mechanical properties and thermal stability. Moreover, the high accessibility of active phase aids eliminating mass diffusion resistance as well as the intra-particle mass transfer problems in reaction

phase [59]. The wide variety of surface functionalization techniques will be discussed in Chapter 2. The organosilanes containing amino groups were reported to modify the surface hydrophilicity and basicity of mesoporous support, controlling the particle size, improving their dispersion and hence increase the catalytic performance in benzyl alcohol selective oxidation [60]. Inspired by this, organosilanes containing amino groups were applied to functionalize CNTs surface in order to improve the catalytic behavior, which will be presented in Chapter 4. Rare earth oxides based heterogeneous catalysts are utilized in a huge number of organic chemistry reactions such as the redox, ketone formation, aldolization, alcohol dehydration, aromatic compounds alkylation, ring-open, coupling reactions and so on owing to their redox, electron donor property and acid-base properties [61, 62]. Various cationic rare earth metallic complexes were synthesized to serve as the catalysts in olefin polymerization reactions [63, 64]. In addition, rare earth oxides have also been applied as either structural or electronic promoter to improve the catalytic behavior of heterogeneous catalysts [65-70]. Ascribed to their lattice oxygen storage capability, the rare earth oxides were applied into automotive catalysts [71, 72], modified catalyst for soot oxidation [73] as well as the industrial catalysts for water treatment [74, 75]. The rare earth oxides used for CNTs surface functionalities will be reported in chapter 5. Considering the high cost and severe conditions of CNTs synthesis, carbon nanospheres greenly synthesized from glucose precursors via hydrothermal method will be reported as catalytic support pretreated by alkali to create abundant surface functional groups in Chapter 6. The intrinsic mechanism of functionalization influence on reaction results will be comprehensively discussed.

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Chapter 2 Literature Review

There is no doubt that deep understanding about the mechanism of alcohol oxidation is of critical importance for designing catalysts. Given a specific oxidation process with already known mechanism, the optimal catalytic properties can be anticipated and the expected catalyst can be designed, synthesized and modified by certain techniques. In addition, the catalyst performance may be determined by the nature of catalytic active center, substrate material, preparation method, reaction conditions and so on. These principles for designing heterogeneous catalyst will be discussed and the advances in selective alcohol oxidation are also exhibited in this chapter.

2.1 General synthetic methods of carbon materials

Activated carbon is generated by carbonization from carbonaceous sources such as coal, wood, coconut husk, nutshells, coir, peat, lignite and petroleum pitch. The carbonization process is carried out under inert atmosphere at temperature ranged from 600 to 900 °C, followed by the activation step consisting of the carbonized material exposed to oxidizing atmospheres at temperature ranged from 600 to 1200 °C. However, if the carbonaceous materials are mixed with certain chemicals such as acid, strong base or salt (sodium hydroxide, calcium chloride, phosphoric acid, potassium hydroxide, and zinc chloride 25%), the carbonization temperature can be relatively lower (450 to 900 °C) with the activation process simultaneously taking place [76]. Whereas, carbon black is conventionally produced from charring organic carbonaceous sources such as wood or bone.

Porous carbon materials are structured with ordered mesoporous silica template. The mesopores can be filled with carbon precursor, which could subsequently be processed to

generate a carbon replica structure, followed with the elimination of silica by extraction. Colloidal particles, colloidal crystals, mesoporous silica and aluminosilica can serve as the template or molds for porous carbons, while sucrose, alcohol, ethylene, propylene, phenol-formaldehyde, acetonitrile, petroleum pitches, resorcinol-formaldehyde resins and other aromatic precursors can act as the carbon precursors. In recent years, nanocasting methods were used with direct soft-templating approach without silica preform. Another method involves the self-assembled surfactants or block-copolymers aggregation for templates and sometimes copolymerization of carbon precursors with alkoxides [57].

CNTs can be synthesized via arc discharge, laser ablation and chemical vapor deposition methods. The process of arc discharge technique is carried out with electric arc between two carbon electrodes distanced 1 mm under an inert gas flow [77], using small pressures ranged from 50 to 700 mbar. A direct current from 50 to 120 A driven by potential around 30 V generates a high-temperature ($>3000\text{ }^{\circ}\text{C}$) plasma within the space between the two graphite electrodes [77] and sometimes the electrodes are made of graphite mixed with catalysts [78]. In the plasma region, graphite electrodes are gradually consumed, fast vaporize and condense to grow CNTs [77]. Principle of the laser-ablation method is analogous to arc discharge. A laser source is employed to make high temperature on carbon object. The sublimed carbon is fast cooled down under an inert gas atmosphere such as helium or argon and produces CNTs [79]. Laser ablation facilitates the chirality (10, 10) structure of CNTs with high purity. Arc discharge and laser ablation methods have the benefit of developing CNTs with superior quality compared with the CVD methods. Nevertheless, arc discharge and laser ablation approaches are challenged with margins in scale-up of CNTs production attributed to their strict reaction conditions.

Figure 2.1 Growth mechanisms for CNTs: (a) tip-growth mechanism and (b) base-growth mechanism.

Figure 2.2 Sketch of a simplest form of CVD setup.

Mass production of CNTs is mainly through the chemical vapor deposition (CVD) technique using transition metallic catalysts [6], e.g., Fe, Ni and Co for cracking the gaseous hydrocarbon feed into carbon and hydrogen before the carbon dissolved into metal particles until the carbon solubility gets the upper limit when the as-dissolved carbon grows and extends outside in the form of crystalized cylindrical network [7]. During the growing of CNTs, the metal nanoparticles could be rooted at the tip [8]

(Figure 2.1(a)) or at the base of CNTs (Figure 2.1(b)) [9], respectively determined by bulk diffusion or surface diffusion, called tip growth or base growth. This is also influenced by strength of the metal-support interactions, that is, CNTs generally grow by the base growth mechanism in correspondence with a strong metal-support interaction, or by the tip growth mechanism according to a weak metal-support interaction. Iron and alumina usually possess high bonding energy with each other. However, detachment of iron from alumina has been observed by Qian et al., implying other reaction parameters, like catalyst, hydrocarbon, pressure, temperature, gas-flow rate, deposition time and reactor geometry, may impact the growth mechanism of CNTs [10]. There are other mechanisms to explain some outstanding phenomena including the endothermic decomposition of methane and “Y” junctions of carbon fibers [7, 11-13]. The formation of either SWNTs or MWNTs is dependent on the size of the metal particles. With particle size about a few nanometers, SWNTs form and while the particle size exceeds 10 nm, it facilitates formation of MWNTs [14]. Many subdivisions of CVD techniques have been established, such as fixed beds [15-19], fluidized beds [20-25], aerosols [26-28], floating catalysts [29-31] and combination methods [32-36] like plasma-enhanced [32, 33] and laser-assisted CVD methods [34-36]. The combined systems based on CVD, laser ablation and arc discharge are able to increase the quality and yield compared to the conventional CVD techniques [37-39]. Nevertheless, they complicate the fundamental scale-up of CNTs mass production due to the harsh operational conditions. Furthermore, the hybrid systems bring in some more new parameters such as ion strength, laser power and the type of plasma in addition to the previous ordinary parameter variables. The rough form of the scheme for the experimental synthesis of CNTs via CVD technique is

shown in Figure 2.2. Typical catalysts for CVD process are prepared on catalytic support using sol-gel methods [40], impregnation procedures [41], metal-organic CVD process [25], or co-precipitation methods [42]. Other methods such as in situ method including the decomposition of volatile metal-organic compounds without substrate within the reactor, also called the floating catalyst method [43]. The catalyst precursors may be solid, liquid or gas state, suitably located in the reactor or fed from outside. In general, the substrates supported catalysts are situated in the high-temperature zone of furnace to catalyze the CNT generation [44]. On the other hand, metal nanoparticles have also been utilized directly in reactors to synthesize CNTs [45]. The growth reaction of CNTs is started by introducing hydrocarbon feed stock, at temperature from 500 to 1000 °C. CNTs grown on catalysts are then collected after the reactor is cooled down to room temperature. When using liquid hydrocarbon such as benzene and alcohol as the carbon source, the liquid feed stock is heated and purged by an inert gas flow which carries the hydrocarbon vapor into the reaction zone. In the case of solid hydrocarbon as the CNT precursor, it is directly located in the low-temperature zone of the reactor. Volatile carbonaceous materials like camphor, naphthalene and ferrocene can directly convert to vapor, and then go on to the CVD process when passing through the catalysts in high-temperature zone [44]. Most frequently used carbon sources include methane [46-48], ethylene [45, 49], acetylene [50, 51], benzene [52], and xylene [53]. Tian et al. reported the benzene pyrolysis at 700 °C to grow CNTs [52], while Li et al. reported the growth of CNTs using pyrolysis of mixture of acetylene and xylene at 800 °C [53]. In those cases iron-based catalysts were employed. For the meantime, CNTs can also be produced from many other precursors such as cyclohexane [54]. SWNTs were first formed by Dai et al.

from carbon monoxide at 1200 °C with molybdenum as catalyst [55]. Afterwards, SWNTs were also produced from benzene [56], acetylene [57], ethylene [58], methane [17, 59], fullerene [60] and so on. A low-temperature synthesis of ultrapure SWNTs from alcohol with FeCo/zeolite as the catalyst has been reported [61], and since then, alcohol became amongst the most popular CNT precursor in CVD method [62, 63]. The advantage introduced in by ethanol as CNTs precursor is that it makes CNTs free of amorphous carbon because of the etching effect of the hydroxyl radical [64]. Vertically-aligned SWNTs were synthesized using MoCo/quartz and MoCo/silicon as the catalyst [65, 66]. Afterwards, Maruyama's group also suggested that intermittent stock of acetylene can assist ethanol in preserving the catalytic activity and hence increases the growth rate of CNTs [67]. Using water-assisted CVD synthesis, the SWNTs grown from ethylene on silicon substrates can be free of impurities [68]. They reported that proper supply of water steam into the reactor served as a weak oxidizer which selectively eliminated amorphous carbon without damaging the CNTs growth. Controlling the ratio of ethylene and water was essential to elongate the effective lifetime of catalyst. In addition, the molecular structure of the carbon feed stock plays a critical role in the morphology formation of the CNTs. Linearly structured hydrocarbons (e.g., methane, ethylene and acetylene) thermally decompose into atomic carbon or linear C₂ or C₃ species, and then grow straight hollow CNTs. For comparison, the cyclic hydrocarbons (e.g., benzene, xylene, cyclohexane and fullerene) grow relatively curved CNTs frequently with bridged structures inside the tube walls [69, 70]. These studies corroborate that the CNT precursor plays a vital role in CNT synthesis. Accordingly, appropriate selection of CNT precursor and the vapor pressure can increase the lifetime

of catalysts, CNT-growth rate, quality and yield. In the CVD synthesis of CNTs, the most frequently-used catalysts are iron, cobalt and nickel owing to the high solubility of carbon atoms in these metals and also the high diffusion rate of carbon in these metals at high temperatures. Moreover, both the low equilibrium vapor pressure and high melting point of these metals enable a wide temperature scale of CVD for a wide variety of CNT precursors. Other considerations include the strong adhesions of Fe, Co, and Ni with the growing CNTs (compared with other transition metals) which lead to higher efficiency in forming low-diameter and high-curvature CNTs such as SWNTs [71]. Solid organometallobenes such as ferrocene, cobaltocene and nickelocene are also frequently used as CNT synthesis catalysts because they release metal nanoparticles without support, making the metal particles entirely exposed to carbon feed stock, increasing the catalytic activity. In general, the metal particle size determines the CNTs diameter. Therefore, controlling the size of metal nanoparticles can control the diameter of CNTs [72]. Catalysts coating on substrates also serve as good technique in achieving uniform CNT arrays [73]. Other metals such as Cu, Mn, Mo, Cr, Sn, Mg, Al, Ag, Au, Pt and Pd were also reported to catalyze a wide range of hydrocarbons pyrolysis for CNT growth [74, 75]. These transition metals are not only efficient catalysts in CVD but also arc-discharge and laser-ablation methods. Noble metals such as Au, Ag, Pt and Pd have low carbon solubility, but can effectively dissolve carbon when the particle size is smaller than 5 nm for CNT growth [76, 77]. The morphology and surface textural properties of support materials largely influence the quality and yield of the as-grown CNTs. Catalysts situated in zeolite nanopores lead to narrow diameter distribution and high yields of CNTs [78, 79]. As catalyst support, Alumina was stated to be a better than silica due to the strong

metal–alumina interaction which enhances high metal dispersion and inhibit metal nanoparticles from agglomeration [80] which results in graphite particles and defective MWNTs [81, 82]. There are also metal-free catalysts for CNT synthesis including nano-diamond [83], metal oxides [84, 85] and semiconductors such as Si, Ge and SiC [86, 87]. The CVD process is performed at a wide range of temperatures from 500 to 1200 °C. The carbon feed stock does not decompose under 500 °C. When the temperature gets to 550 °C, very short tubes are developed at very low growth rate, which would abruptly increase at 600 °C. TEM observation discloses that the CNTs diameters increase when the temperature increases. Pure CNTs free of metallic impurities are formed at 750 °C, implying that the catalyst-support interaction is strong enough to keep the metal particles firmly attached to the support at low temperatures. Thus, the CNTs growth is mainly via the base-growth process. As the temperature increases, the CNTs gradually incorporate more metallic impurities, usually encapsulated at CNTs tips, inferring the presence of both tip-growth and base-growth mechanism at critical temperatures and the inhomogeneous dispersity of metal particles. The larger metal clusters may leave the substrate with the growth of CNTs. When the temperature is above 750 °C, the CNTs diameter and diameter-distribution increase radically since the metal atoms aggregate into larger clusters resulting in thicker CNTs at high temperature and also are influenced by the higher carbon precursor pyrolysis rate which results in thicker walls. From 850 °C and onward, more SWNTs begin to form when the temperature increases. High temperature favors SWNTs implies the high formation energy attributed to its small diameter, high curvature and high strain energy. For comparison, low temperature favors the formation of MWNTs with the optimized temperature of 650°C with FeCo/zeolite catalyst. At such

a low temperature, the formed CNTs are almost free of metallic impurities. On the other hand, the optimal temperature for the formation of SWNTs is 900 °C using the FeCo/zeolite catalyst [78]. The pressure of gaseous carbon precursor could be controlled by the gas flow rate [88]. In cases of liquid hydrocarbon, the vapor pressure is controlled by heating to a certain temperature before it is purged into the reactor [89]. For a solid hydrocarbon precursor such as camphor, the vapor pressure is controlled by optimizing three parameters: camphor mass, evaporating temperature and the flow rate of carrier gas [78].

A “green” synthetic approach free of toxic reagents and organic solvents has been established to transform the readily prepared precursors including glucose [90-92], starch [93] and cyclodextrins solutions [94] to generate carbon spheres by simply using hydrothermal vessels at the temperature ranged from 160 °C to 180 °C. The diameters of carbon nanospheres are influenced by temperature, reaction duration and the concentration of precursor solutions. At constant temperature and reaction time, diameter and size distribution increase with the increase of reaction time and peanut-like or other irregular shapes occur at long reaction duration. High concentration of precursor solution usually leads to large diameters and broader size distributions [91, 95]. Concerning temperature issues, Li et al. reported the diameter decreased when the temperature increased from 180 °C to 190 °C while broken or irregular shapes of carbon nanospheres appeared at 210 °C using 0.3 M glucose solution [95]. According to the discussion of temperature, reaction time and precursor concentration factors, the diameters and size distribution of carbon nanospheres can be well controlled by controlling these three parameters.

2.2 Functionalization approaches of carbon materials

Direct functionalization of carbon materials is realized via one step reaction. Activated carbon was mixed with amines, alcohols or thiols for solvent-free reaction with microwave assistance, where the organic groups directly link to the double bonds. The microwave reactions were carried out under moderate conditions since the reaction durations were less than 100 min and temperatures beneath 200 °C [96]. Cyclic nitrones can be covalently bonded to the CNTs surface via the cycloaddition reaction between cyclic nitrons and CNTs under a continuous sonication condition [97]. Carbon black directly functionalized with phenyl, nitrophenyl and phenylazoaniline was obtained by reaction with aniline precursors, nitrite and acid [98].

Numerous methods are capable of generating amine-functionalized carbons, convenient for subsequent formation of amide linkages through amidation reaction or modify the surface properties. Amino groups can be introduced via reduction of carbons pretreated by nitrate together with acetic anhydride, sulfuric acid and fuming nitric acid [99]. The reduction reaction forming amino groups from the nitro groups was realized by the addition of ammonia and sodium hydrosulfite. Diamines treatment can efficiently realize the amine-functionalization on CNT surface as well, using a microwave assisted approach [100] or by diamines reacting with preexisting acyl chloride groups. It has also been reported that nitric acid pretreated carbon fibers can be grafted with amine groups via reaction with tetraethylenepentamine, forming single or multiple bridges on carbon surface [101].

Surface acidic groups can be converted into basic surface groups such as amine and pyridine groups via high temperature treatment under the anhydrous ammonia

atmosphere. This treatment resulted in corrosion of carbon surface as well. In the case of carbon fibers, samples burdened the weight loss meanwhile the nitrogen content, specific surface area, pore volumes and pore diameters have been enlarged. Direct reaction between ammonia and phenolic fiber precursors is possible, proving the ammonia-etching effect on the carbon fiber surface [102].

Free radical reactions initiated by UV exposure are also applied for covalently grafting functional groups onto carbon surfaces. This photochemical reaction undergoes when carbon in hydrogen plasma with alkene attaching to C-H terminated carbon surface under the extended exposure under UV light [103]. In a practice of this technique, a thin carbon film was grafted with trifluoroacetic-acid-protected 10-aminodec-1-ene and the functional groups were used as anchoring sites for DNA after removing the protecting groups [103]. This approach provides a covalently stable functionalized interface, functioning well for either low-temperature or high-temperature biosensing process on carbon surface.

Electrochemical grafting of functional groups onto carbon surface is possible in the cases of diaryliodonium compounds. Taking glassy carbon electrodes for example, the functional groups grafted via this process ranged from electrophilic to nucleophilic groups, including carboxylic acids, nitro, chlorine, bromine, hydrogen and methyl groups [104]. Another grafting method has been established for glassy carbon associated with the electrochemical functionalization using 4-aminobenzoic acid [105]. Functionalization of hydroquinone onto CNTs through phenol electro-oxidation method was reported. Upon the nitric acid treatment of CNTs, this material was affixed to the working anodic electrode and immersed into the liquid mixture of phenol and phosphate buffer solution.

Then it was cycled with the potential ranged from -0.2 to 0.6 V at the rate of 50 mV s^{-1} for twenty cycles using Ag/AgCl as the reference electrode. After rinsing and moving to another fresh pH 7 phosphate buffer solution for the stabilization via potential cycled 20 times from -0.2 to 0.6 V using Ag/AgCl as the reference electrode, the surface coverage of hydroquinone was determined by the cyclic voltammetry graph, the integration of peak area of the corresponding surface-confined redox peak.[106]

Oxygen-containing groups like ketone, phenol, lactone, carboxyl group, ether, acid anhydride, etc., are usually generated by controlled oxidation on CNTs surface [107], taking advantages of their several usages. The extent of oxidation is determined by the strength of oxidants and oxidation conditions. Common oxidants include nitric acid, hydrogen peroxide, permanganate, hypochlorite, persulfate, hypochlorite, chlorates, dichromate, oxygen, ozone and nitric oxide [108-111]. Whereas the oxidation condition must be appropriately controlled in order to prevent overly corrosion and structure disruption of the CNTs backbone. Mild oxidant makes it possible to adjust the surface properties [112]. Different types of oxidants or different oxidative conditions do make a difference on the proportion of each kind of surface groups. For instance, air oxidation generates more phenol and less lactone or anhydride groups [113], while gaseous nitric acid oxidized CNTs possess more C=O than liquid nitric acid oxidized CNTs [114]. Nevertheless, these oxygen-containing groups are not stable at high temperature. The amount of oxygen-containing groups obviously decreases with the increase of temperature higher than a certain value [115], releasing CO_2 , CO and H_2O molecules, which can be examined by temperature programmed desorption (TPD) [116]. Heat treatment favors the decrease of surface acidic groups (like carboxylic acid, lactone and

phenol) and increases of surface basic groups (like chromene, pyrone, quinone and hydroquinone), since the basic groups are formed as a result of the decomposition of acidic groups under an inert atmosphere at high temperature [117]. The most widely used oxidant for carbon materials is concentrated or diluted aqueous nitric acid [110, 114, 116-121], which is also a frequently used step for CNTs purification removing amorphous carbon and metallic impurities [115]. Nitric acid is an efficient and controllable oxidant for the formation of surface groups, simply by controlling the treatment temperature, acid concentration and oxidation time. Hence, this oxidation process has also been employed for surface functionalization of CNTs generating oxygen-containing groups especially carboxyl groups and surface charge [114, 116-118]. Nevertheless, excessive oxidation results in structural degradation and oxidation debris which is known to influence dimensions of CNTs, surface properties and the chemical and biological dispersion and stability [122]. In the cases of longer nanotubes, the oxidation debris might bring about bundling of CNTs by sticking nanotubes to each other, and removal of the debris would favor the dispersion of the tubes. While for short nanotubes, oxidation debris are likely to favor sufficiently dispersed, micelle-like structures in various media [123].

An effective approach to dope heteroatoms such as boron and nitrogen on carbon nanotubes is usually obtained during the one-step synthesis. In the case of synthesizing N-doped nanotubes, the mixture of hydrocarbon and ammonia [124] or hydrocarbon and organic amine [125] or simply pure organic amine [126] are adopted as the carbon and nitrogen source, slowly flowing with argon into a heated quartz tube furnace with a quartz or ceramic boat inside which is filled with iron-containing catalyst [124-126]. For the synthesis of B-doped CNTs, organic borane is used instead of the organic amine,

following the same chemical vapor deposition (CVD) process as the synthesis of N-doped CNTs [125]. The phosphorous doped CNTs are synthesized via the same CVD method using organic phosphine as the phosphorous source instead [127]. Similar CVD methods are reported for the sulfur doping on CNTs surface as well [128]. A detonation-assisted CVD technique is also adopted to prepare compartmentalized bamboo-like N-doped CNTs, using CNTs as the catalyst, picric acid and melamine as the carbon and nitrogen source. Mixture of CNTs, picric acid and melamine are put in a sealed stainless steel pressure vessel, followed by the detonation induced by external heating to 310 °C, occurring on a microsecond shock wave at 40 MPa pressure and 900 °C temperature [129]. Nitrogen plasma deposition is also employed as a technique to generate N-doped CNTs [130-132]. Arrays of aligned N-doped CNTs can grow vertically on Si (100) facets via aerosol-assisted catalytic chemical vapor deposition (CCVD) method. A quartz tube inserted into a heated tubular reactor is filled by nitrogen gas and silica substrate is located in central part of reactor, while the mixture of ferrocene, and metal carbonyl dissolves in acetonitrile is injected into tube reactor. The pyrolysis is performed under a nitrogen flow and aligned N-doped CNTs are formed vertical on Si substrate [133]. Instead of Si, alumina can serve as the substrates for growth of aligned N-doped CNTs as well [134]. Besides, graphene can also be utilized as the substrates for synthesizing arrays of aligned N-doped CNTs, using reduced graphene oxide supported Fe₃O₄ as the catalyst instead of the ferrocene, and metal carbonyl [135].

The sulfonation is conducted by carbon materials contacted with the vapor from 5 mL of 50 wt.% SO₃/H₂SO₄ at 60 °C for 48 h in a Teflon-lined autoclave, then washed with hot deionized water (>80 °C) to remove all species that are physically adsorbed until the

sulfate ions are no longer detected in the filtration water [136]. Another technique of sulfonation is through reacting with ammonia sulfate. Ammonia sulfate solution was agitated with a proper amount of CNTs, before heating at 235 °C for 30 min, decomposing to generate SO_3 which forms surface $-\text{SO}_3\text{H}$ groups [137, 138]. Sulfonation of carbon materials has been employed for creation of environmentally friendly solid acid catalysts.

Figure 2.3 Grafting reactions to functionalize CNTs surface via covalent bonds. See the text and specific references for more details.

The broadest range of surface functional groups on CNTs is possible by grafting approach (Figure 2.3). In many of these methods, the CNTs surface already has a surface functionality, which can be further substituted by organic groups. The preexisting

functionalities are usually formed by oxidation of CNTs via boiling with nitric/sulfuric acid. In other cases, functional groups are bonded directly on CNTs surface. On oxidant treated CNTs, carboxyl groups react with thionyl chloride to form acyl chloride groups, which is a versatile intermediate for a wide range of organic groups. The acyl chloride can react with cysteamine by the amidation reaction, grafting thiol groups. With the coordination of thiol groups, metal particles may attach onto the sidewall of CNTs, serving as sensors and catalysts [139]. Another example of the usage of acyl chloride is to graft chitosan on CNTs surface in order to obtain novel CNT-chitosan composite which is potential for applications in bone tissue engineering. First, 0.5 g of degraded chitosan was reacted with 0.02 g of $K_2S_2O_8$ for 20 h before adding 0.0555 mol of lactic acid for another 2 h, and then quenched by adding 10 mL of tetrahydrofuran followed by freeze-drying. The dried sample was rinsed with methanol and the as-prepared product was reacted with the acyl chloride on pretreated CNTs surface in acetic acid at 75 °C with vigorous stirring for 24 h before rinsing three times with acetic acid removing unreacted chitosan [140]. L-lysine can react with acyl chloride via amidation reaction to form lysine or poly-lysine grafted CNTs, which is proved to have enhanced the wettability to deposit and disperse titanium dioxide nanoparticles and thus obtain improved photo-catalytic activity for methyl orange degradation reaction.[141] Besides amidation reaction, metal organic salts are reacted with acyl chloride groups. For instance, magnesium chloride dithiopropanoate reacted with acyl chloride groups on CNTs surface forms CNTs chain-transfer agents for application in reversible addition-fragmentation chain-transfer polymerization [142]. Taking advantage of the esterification based on the carboxyl groups on CNTs surface, a broad range of groups can be grafted. For instance, the surface

imidazolium functional groups have been obtained and this imidazolium functionalized CNTs have been used for the preparation of a nanohybrid catalyst containing organometallic complexes which are highly efficient and effective heterogeneous hydrogen transfer catalysts for the cyclohexanone reduction reaction with 2-propanol as the hydrogen source [143]. The hydroxyl groups formed from oxidation of CNTs are always used for silane-grafting onto CNTs surface. Aminosilane, especially the 3-aminopropyltriethoxysilane is a frequently used modifier, capable of improving the modulus, tensile strength and elongation at break of CNT reinforced composites [144-147] and sometimes used to construct amide linkages or hydrogen bonds. The 3-aminopropyltriethoxysilane functionalized CNTs is also reported with promising CO₂ absorption capacities and selected as the CO₂ adsorbents for the study of cyclic CO₂ capture system [148, 149]. Calculated amount of 3-aminopropyltriethoxysilane dissolved in acetone was mixed with oxidized CNTs dispersed in water with vigorous stirring at 80 °C for 30 min. The silane-functionalized CNTs were separated by filtration using distilled water and acetone before drying overnight [144, 145]. In addition, 3-aminopropyltriethoxysilane has been bonded onto CNTs surface via a post-synthesis method for further loading of Pd nanoparticles in order to increase the surface basicity and hydrophilicity for better dispersion of Pd particles onto the functionalized CNTs and thus to obtain improved catalytic performance for the solvent-free oxidation of benzyl alcohol using O₂ [150]. Silanes like 3-Glycidoxypropyltrimethoxysilane [151], γ -glycidyloxypropyltrimethylsilane [152] and so forth are adopted as coupling agents for better dispersion, interfacial interaction and reinforcement effect of CNTs in nanocomposites [151, 152]. Moreover, The well-dispersed silane-assisted Pt and Pt-Co

alloy deposition on CNTs exhibit good electrochemical catalytic behavior as cathodes in a proton exchange membrane fuel cell [153]. In spite of the reflux treatment with oxidants, the functionalization of CNTs at the preexistence of surface functionality can be realized on CNTs pretreated by air or O₂ plasma atmosphere to create oxygen-containing groups as well [154-156]. O₂ plasma is an effective treatment for CNTs surface without resulting in any severe damage and leaves CNTs intact by tuning the plasma treatment conditions [154]. These introduced oxygen surface species are used to immobilize biomacromolecules such as enzyme, antibody and deoxyribonucleic acid for sensing or catalysis applications. [155, 156]

Diazonium compounds have been utilized for direct aryl or aryl derivatives grafted onto CNTs. It is a versatile approach by using diazonium compounds with almost any need groups bonded on the aryl species.[157] In a typical treatment process in aqueous solution, the mechanism for diazonium salts reacted with CNTs is a free radical chain reaction mostly initiated by the diazoanhydride homolytic decomposition and slightly through direct oxidation of CNTs by diazonium compounds. Once the aryl radicals have been formed, they are covalently bonded to CNTs. In a testing experiment investigating the reaction mechanism, diazonium compound was dissolved in water before adding to a proper amount of SWNTs aqueous solution in a quartz cuvette at 27 °C observed by visible or near-infrared spectroscopy simultaneously [158]. Nevertheless, the diazonium salts do not have to be prepared before the functionalization reaction since the in-situ generation of diazonium compound during CNTs functionalization can be realized via the simple one-pot reaction of CNTs, aniline derivatives and nitrite [157, 159-164]. For example, heptafluorooctyl phenyl groups functionalized CNTs were prepared

following this process: 460 mg of heptadecafluorooctyl aniline were dissolved in 50 mL of acetonitrile while 250 mg of CNTs are dispersed in 50 mL of DMF and subsequently make them mixed together, heated to 60 °C under vigorous stirring then with the addition of 2 mL isoamyl nitrite. The reaction continued at 60 °C overnight followed by vacuum filtration and rinsed by DMF and methanol [161].

Prado's reaction, briefly the azomethine ylides 1, 3-dipolar cyclo-addition forming pyrrolidine rings, has been reported to be an interesting functionalization process on surface of carbonaceous materials [165-168]. The formed pyrrolidine rings consist of two covalent C–C bonds belonging to the carbon surface, making this grafting based on the stable bonding of functional groups. This technique is also applied for CNTs functionalization [169-174]. In a typical reaction for instance, CNTs was dispersed in 1,2-dichlorobenzene first. Under argon atmosphere, 3-thiophenecarboxaldehyde was added to the mixture, followed by a calculated amount of N-methylglycine added little by little over 5 days. After finishing the adding of N-methylglycine, the reaction was left to continue for another 24 h before cooling, filtration, washing and drying [170, 173].

Besides organic molecular functionalization of CNTs surface, a broad range of approaches have been established to functionalize CNTs surface with nanoparticles. These techniques can be mainly classified into four categories: nanoparticle dispersion on functionalized CNTs, physiochemical approaches, electrochemical deposition and electroless deposition [175]. Incorporation nanoparticles on CNTs could be defined as a method of functionalization. The introduction of nanoparticles favors the extension of the CNTs applications and presents new features such as electrochemical and catalytic activities. Metal oxides and mixed metal oxides are formed by precursors bound on CNTs

with the presence of surface functional groups for anchoring metal ions or metal nanoparticles [175]. This method is also named as impregnation, a simple and inexpensive methodology, where the most commonly utilized functional groups on CNTs is carbonyl and carboxyl groups via nitric acid or nitric/sulfuric acids mixture treatment of CNTs before the bound of precursors. Without surface functional groups as anchoring sites, the nanoparticles on perfect CNTs surface through impregnation process merely have the particle-support physical interaction which may easily result in leaching and loss of the nanoparticles. Taking MnO_2 as an example, the CNTs was first oxidized with nitric acid, functionalized with oxygen-containing groups. 0.5 g of functionalized CNTs dispersed in 50 mL of toluene and calculated amount of manganese (II) acetylacetonate dissolved in 50 mL of toluene were separately refluxed at 110 °C for 5 h with a nitrogen flow to remove moisture before the two slurries mixed in a larger flask and refluxed at 110 °C overnight. The slurry was cooled to room temperature, filtered, rinsed and dried followed by annealing under nitrogen atmosphere at 400 °C for 6 hours [118]. This manganese oxide functionalized CNTs are applied as promoted catalytic supports for palladium catalysts in aerobic selective oxidation of benzyl alcohol [118]. A CeO_2 and CuO mixed metal oxides were deposited on CNTs with nitric acid pretreated. CNTs were first refluxed in a concentrated nitric acid at 140 °C for a day. $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (2 mmol), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.5 mmol) and pretreated CNTs (0.08 g) were dispersed in pyridine (30 mL), sonicated for 30 min. The suspension was transferred into a Teflon-liner autoclave (50 mL), and then located in an oven at 180 °C for 24 h. After cooling down to room temperature, it was rinsed several times before drying at 100 °C for 12 h and annealing at 200 °C for 2 h. As a catalyst, the $\text{CeO}_2/\text{CuO}/\text{CNT}$ nanowires have a much more

promising catalytic activity for the CO oxidation than that of either CeO₂/CNT or CuO/CNT nanowires [176]. Highly dispersed RuO₂ nanoparticles on CNTs were prepared via impregnation method with the assistance of NaOH to control a stable pH at 7. 10 mg of nitric acid pretreated CNTs was suspended in 30 mL of water and treated by sonication for 3 h. A proper amount of RuCl₃•3H₂O was dropped to the CNT suspension. NaOH was added to control the pH value of the suspension stable at 7 followed by the mixture refluxed at 120 °C proceeded for 6 h. After cooling down, the suspension was filtered, rinsed, dried, and then calcinated at 150 °C for 6 h under inert atmosphere. The as-prepared highly dispersed RuO₂/CNT composites are applicable in fields of superior electrode materials and super capacitors [177]. The deposition of metal nanoparticles such as palladium can also be realized in similar ways with the annealing step replaced by the hydrogen gas reduction treatment [118]. There are various physical methods used to prepare nanoparticles deposited on CNTs. The physical techniques include evaporation deposition, sputtering deposition and ion and electron beam irradiation deposition and they possess the control over the size, shape, dispersion and uniformity of the nanoparticles. Evaporation deposition is carried out by impregnating the CNTs in an aqueous solution containing metal precursor before the removal of water by evaporation and the solid sample is obtained after drying at 100 °C for 12 h. Calcination of the solid sample at around 400 °C for 4 h or in air yields nanoparticle attached on CNTs [178]. Sputtering deposition generates uniformly dispersed metal nanoparticles by choosing proper metal cathodes, monitoring the electric current and sample exposure duration. Ion or electron beams irradiation deposition is performed under γ -irradiation and electron beam irradiation to disperse nanoparticles homogenously [175]. Metal organic vapor

deposition is another solvent-free methodology applied to attach nanoparticles directly onto surface of CNTs. The deposited nanoparticles are evenly dispersed with sizes in the scale of 2 to 4 nm. A volatile salt of metal catalyst mixed with CNTs generates a homogeneous mixture [179]. This mixture placed under an inert atmosphere is then heated until the salt decomposes and allows the metal nanoparticles to deposit onto CNTs surface [180]. Since the metal organic vapor deposition method includes fewer steps, this technique can be applied to form homogeneously dispersed metal nanoparticles on CNTs. Electrochemical deposition process enables the synthesis of metal nanoparticles attached onto CNTs via reduction of metal complexes such as auric chloride acid, platinumic chloride acid and ammonium platinumic chloride by electrons on cathodes [175]. The CNTs behave like conducting wires and supports for metal nanoparticles deposition however without reactivity with the metal precursors. Altering the parameters including the content of metal precursors, nucleation potential and process duration favors the variation in the size and the uniformity of the metal nanoparticles on the surface of CNTs [175]. Electrochemical deposition possesses the advantage in generating extremely pure metal nanoparticles functionalized on CNTs with strong metal-support interactions, within short process duration [181]. On the contrary, the disadvantage of the electrochemical deposition methodology involves the formation of large metal nanoparticles on CNTs surface, usually ranges from 10 to 100 nm [182]. Preparation of nickel nanoparticles on carbon nanotube has been reported. Nickel loading was carried out on functionalized and pristine CNTs respectively through electrochemical deposition. Nickel-CNTs hybrids synthesized from functionalized CNTs with acid treatment exhibited more uniformly dispersion of nickel particles than those on the surface of pristine CNTs [183]. Altering

deposition duration and electric current has a significant effect on the morphology of nickel oxide on CNTs. And homogenously dispersed nickel oxide particles with size ranging from 15 nm to 30 nm on CNTs have been reported [184]. Electroless deposition of nanoparticles on CNTs depends on a reduction chemical process with the presence of reducing agents. Direct reduction reaction takes place between the metal precursors and CNTs during the electroless deposition process [175]. However, the application of electroless deposition is restricted by the principle that redox potentials of metal ions have to be higher than that of CNTs and thus can be reduced to nanoparticles on CNTs support [185]. This drawback has been overcome by a substrate-enhanced electroless deposition procedure which involves the supporting CNTs with a metal substrate possessing a lower redox potential than the targeted metal precursors [175]. A Pt/Ru/Mo/graphene-CNTs catalyst has been synthesized via chemical reduction of metal precursors with sodium borohydride as the reducing agent at room temperature [186].

2.3 Applications of functionalized carbon materials

Oxidized CNTs are usually adopted as purified catalytic support [115], providing oxygen-containing groups as anchoring sites of functionality immobilization during further surface functionalization [118]. The presence of oxygen-containing groups facilitates smaller metal nanoparticles, enhanced metal support interaction, higher electrochemical active surface area and therefore higher catalytic activity and selectivity are obtained in cinnamaldehyde hydrogenation reaction, in comparison with the surface groups eliminated CNTs support [115]. However, compared to oxidized CNTs support, the promoted CO electro-oxidation activity in CO stripping voltammetry is determined by the high conductivity of pristine CNT support which means oxygen-containing surface

groups may hamper the electro-oxidation of CO molecules and lead to higher potential for CO oxidation [115, 187].

Doping of heteroatoms is an efficient method to fine-tune the structural and electronic properties of nanotubes [188]. Nitrogen atoms can contribute additional electrons and faster electron transfer, leading to the easy occurrence of protonation of nitrogen, which can induce negative charges on adjacent carbon atoms, and thus enlarge its electrode capacitance and make N-doped CNTs a great super capacitor [133]. The enhanced electron density endows N-doped CNTs good field emission characteristics for field emitter [189]. Besides improving electron transfer kinetics and higher conductivity, nitrogen doping also increased the electrochemically active surface area of CNTs for the usage as electrodes in thermo-electrochemical cells [190] or fuel cells [191]. Nitrogen doping and its disruption of the carbon lattice can impact electronic properties and thus the nitrogen concentration greatly determines the electro capacitance, conductivity, density of state and morphology of the N-doped CNTs [192]. The pristine, N-doped and B-doped CNTs possess different surface vacancies and different interactions with gas molecule which can be applied for gas sensing detector [125, 193]. The heteroatoms also bring in some defects and active sites onto the surface of nanotube, resulting in greater reactivity than pristine CNTs [188]. The N-doped carbon nanotubes were utilized for the immobilization of hemoglobin, and the functionalized electrodes exhibited favorable bio-electro catalytic activities for the reduction of hydrogen peroxide [194] and oxidation of glucose [195]. Additionally, N-doped carbon nanotubes modified glassy carbon electrodes have been proved to have promising electro-catalytic performance for the oxidation of dopamine and ascorbic acid [196]. The Nitrogen- and Phosphorous-doped

CNTs are active metal-free catalysts for the aerobic oxidation of cyclohexane owing to the expedited electron transfer between graphitic sheets and reactive radical sites, which can be ascribed to the n-type dopants such as N or P functionalities. However, boron behaves on the contrary because of its electron-deficiency [127]. Moreover, the N-doped CNTs demonstrate obvious basic property attributed to the pyridinic nitrogen, although there are many other nitrogen types like oxidized pyridinic nitrogen, quaternary nitrogen and pyrrolic nitrogen, making N-doped CNTs metal-free catalysts for Knoevenagel condensation [197], acetone aldol condensation, acetic acid decarboxylative condensation, hydrogen sulfide selective oxidation and oxygen reduction reaction [198]. For catalyzing oxidative dehydrogenation of propane, graphitic nitrogen plays a paramount role in improving CNTs activity through facilitating the activation of oxygen and diminishing the total activation energy of the reaction [199]. Doping sulfur via CVD method forms distorted sidewalls on CNTs, since sulfur favors the generation of pentagon and heptagon carbon rings. Sulfur dopants create more active sites on CNTs surface for utilities in catalysis. In addition, sulfur dopants can improve the nitrogen-doping content on CNTs, as a result of heterocyclic rings, which facilitate the enhancement of nitrogen-doping. The magnetic property of CNTs is also enhanced by sulfur-doping, attributed to the improved encapsulation of ferromagnetic species. And the enhanced soft magnetic property of CNTs is promising for the applications in the fields of magnetic data storage and electromagnetic wave-absorbance [128]. Doping of sulfur and/or selenium in nitrogen-doped graphene–CNT composite also generates metal-free catalysts for oxygen reduction reaction. Particularly, the additional selenium-doping exhibits significantly enhanced oxygen reduction reaction activity with high methanol tolerance as well as durable

stability in acid media in contrast to Pt/C [200, 201]. As catalytic supports, both the N- and B-doping of CNTs are favorable to metal such as platinum adsorption on their surface with different mechanisms. Dopant nitrogen atoms enhance metal adsorption via activating carbon atoms adjacent to nitrogen atoms, as a result of the strong electron affinity to nitrogen. In contrast, the improved platinum adsorption on boron-doped CNTs is primarily ascribed to the strong hybridization between metal d orbital and boron p orbital, causing direct bonding between the platinum and boron atoms [202]. The platinum adsorbed on N-doped CNTs surface presents promising catalytic performance for methanol electro-oxidation [203]. N-doped CNTs supported iron catalyst turns out to be excellent Fischer–Tropsch catalysts with high selectivity for the short-chain olefins, decreased chain growth probability, and superior long-term stability [204]. Moreover, the nitrogen species on CNTs can act as anchoring spots for the bimetallic particles immobilization and highly dispersion. It is substantiated by the nitrogen-doped CNTs as a favorable support for PtRu/N-CNT catalyst for electro-oxidation of methanol owing to the better dispersion of bimetallic nanoparticles and the excellent electrochemical properties of N-doped CNTs [130]. Metal particles supported on N-doped CNTs possess higher catalytic activity than CNTs. The general order of catalytic support efficiency is ranged as N-doped CNTs > CNTs > conventional supports. N-doped CNTs enhances the electron density, meanwhile increases the basicity and the presence of CNT-N⁺:H protonated sites. The expedited electron transfer from N-doped CNTs to metal particles leads to metal activation and the formation of metal-support chemical bonds in some cases. Besides, the CNT-N⁺:H protonated sites can serve as immobilization spots for metal particles [205].

Sulfonated Pt/CNT catalyst displays better electro-catalytic performance than unsulfonated counterpart, indicating that sulfonation is an efficient way to improve the behavior of Pt/CNT-based electrodes [138]. The surface sulfonation increases proton conductivity as a result of the decrease in charge transfer resistance in oxygen reduction reaction of the electrochemical impedance spectroscopy characterization [206]. Besides, some organic sulfonic acids functionalized CNTs possess well-tuned interfacial properties, thus eliminate aggregation and assist CNTs doping into the PbO₂ film which obtains higher electro-catalytic activity and prolonged electrode service life [207].

The as-synthesized heptadecafluorooctyl phenyl functionalized CNTs related composites possess promising suitability for sensor applications, in contrast to CNTs without functionalization [161]. In other cases, functionalization using diazonium compounds undergoes following the electrochemical methods, CNTs as the working electrode while diazonium compounds inside the KCl and HCl aqueous electrolyte [208-211]. The functionalized CNTs via electrochemical diazonium grafting were used to enhance the ionic diffusion effect of the CNT membranes [210, 211]. Diazonium salts functionalization favors the electron transfer kinetics across a wide range of potentials. Through adjusting the electrochemical conditions, applied potential as well as the type of diazonium salt, it is possible to get an electrochemical charge transfer rate at a kind of conductive SWNTs that is 104 times of that at an semiconducting SWNTs [209]. Application of diazonium salts in spinning of CNTs is assisted by the addition of surfactant in order to form a negatively charged CNTs surface for better interaction with the positively charged diazonium [212, 213]. The CNT yarns with diazonium salt functionalization demonstrate better tenacity and strength against the untreated CNT

yarns [212]. Additionally, the diazonium salt grafted carboxyphenyl groups can react with multifunctional reactive compounds such as hexa(methoxymethyl) melamine, constructing highly crosslinking polymerization within the yarns, enabling higher tensile strength, Young's modulus and therefore load transfer efficiency [213].

The Prado's reaction functionalized CNTs with specific organic groups has particular application. For instance, the zinc porphyrins covalently grafted onto the side walls of SWNTs via Prado's reaction favor the efficient intramolecular charge separation and intermolecular electron transfer and therefore leads to applications in solar energy conversion [174].

2.4 Functionalized carbon materials for heterogeneous catalysts

Owing to the chemical stability, electronic conductivity, thermal stability, capability to functionalize with chemically or electrochemically active species, CNTs are promising materials for applications in catalysis. Plenty of target reactions have been catalyzed by CNT-supported mono or multi metallic nanoparticles. These days, the entire humanity is facing the grim challenges brought by the approaching energy crisis along with severe environmental problems. It is the scientific community's obligation to develop clean and sustainable energy resources as well as environmental purification techniques that can ease the current difficult situation. As part of the solutions, state-of-the-art technologies, such as photodegradation, photocatalytic water splitting, photoelectrochemical cells, electrocatalytic H₂ generation and many other strategies have been developed and thoroughly studied. At present, CNTs are playing more and more important roles in relevant research fields. CNTs alone or their composites can be developed into various efficient catalysts that are suitable for diversified sustainable energy and environmental

engineering applications. Alternatively, CNTs can also be used as scaffolds or structural supports in the development of other catalyst candidates. At current stage, it's also important to review the milestones achieved by using CNTs in these promising research areas.

In hydrogenation reactions [214-222], the advantages of CNTs support can include eliminating the inner diffusion effect of reactants or products [214], the strong metal-support interactions [214], π - π interaction between CNTs and aromatic reactants [115] and enhanced reducibility of the catalysts [223]. Functionalization of CNTs has a significant impact on catalytic performance. After the nitric acid treatment of CNTs, surface oxygen-containing groups may retard the reduction of platinum nanoparticles supported on pre-oxidized CNTs, where the surface oxygen-containing groups strongly stabilized the cationic platinum species [224]. Removal of oxygen-containing species from CNTs suppresses acid-catalyzed side reactions and expedites electron transfer between CNTs and platinum nanoparticles, consequently improving both the activity and selectivity in cinnamaldehyde (CALD) hydrogenation reaction [115]. Whereas, further functionalization with iron and cobalt nanoparticles on CNTs surface after the removal of oxygen-containing groups leads to metal-metal synergic effect and therefore elevate the activity and selectivity in CALD hydrogenation [115]. CNTs surface functionalization with silica layers via the hydrolysis of 3-aminopropyltriethoxysilane and tetraethoxysilane improves the durability of Ru/CNT catalyst during the repeated hexane hydrogenation reaction [225]. Polyaniline (PANI) functionalized CNTs supported palladium nanoparticles are stably and uniformly distributed due to the Pd-N interactions. The Pd-PANI/CNT catalyst displays high activity and selectivity for the hydrogenation

of phenol toward the cyclohexanone, since the catalytic activity is associated with the conductivity of PANI/CNT, while the selectivity toward cyclohexanone is attributed to the nitrogen-containing basic sites of PANI/CNT. In addition, the easy adsorption of phenol in a “nonplanar” fashion over nitrogen-containing basic sites leads to the active and selective phenol hydrogenation toward cyclohexanone [226].

CNTs have been investigated for CO/H₂ conversion reactions such as Fischer-Tropsch synthesis [227-241], methanol [242] and higher alcohol synthesis [243-246]. In contrast to conventional support material such as silica and alumina, CNTs as catalytic support could remarkably reduce the duration of induction period, improve the reducibility of active phase and promote the catalytic activity and stability for Fischer-Tropsch synthesis [227, 229]. Compared to activated carbon and MgO, CNTs supported cobalt has the highest CO conversion and Co/CNTs-MgO enhances the selectivity toward C₅+, the most valuable Fischer-Tropsch synthesis products while reduces the selectivity toward CH₄, the most unwanted product [241]. Compared with Fe supported on activated carbon catalysts, Fe/CNT systems possess lower selectivity toward methane and high selectivity to olefins [247]. The selectivity of Co/CNT catalyst can be largely altered if manganese promoter is applied. The C₅+ selectivity is significantly higher while the methane selectivity is diminished and a higher olefin-to-paraffin ratio is attained compared to Co/CNT without promoter at 1 bar. The manganese promotion effects are dependent upon pressure, since the alteration in selectivity can be less pronounced or reverted at a pressure as high as 30 bar [248]. CNTs surface functionalization of oxygen-containing groups through acid treatment opens the caps, enlarges BET surface area and introduces plenty of defects and acidic functional groups which facilitate diminished

cobalt particle size and size distribution and enhance dispersion of cobalt nanoparticles. Furthermore, the reducibility of catalysts increases by 10% and 50% with acid treatment at 25 ° and 100 °C respectively and most of the nanoparticles have been homogeneously dispersed inside the nanotubes since the cobalt precursor can be introduced into the tubes by capillary forces of CNTs after acid treatment. The Fischer-Tropsch activity and CO conversion are both strongly increased after the acid treatment of CNTs support [249]. Acid treatment of CNTs support also improves the catalytic performance of Fe/CNT catalysts for Fischer-Tropsch synthesis ascribed to the similar reasons [234]. Confinement of cobalt nanoparticles inside CNTs hinders deactivation caused by sintering and cobalt oxidation. However, confinement of reactants or intermediates inside the tubes may increase the reaction time contacting the catalysts, incurring the formation of longer-chain hydrocarbons [230]. The Co-in-CNTs catalyst possesses the selectivity to C₅⁺ of 15.7% and 23% after hydrogen treatment at 300 °C and 400 °C respectively, whereas the Co-on-CNTs catalyst possesses the selectivity to C₅⁺ of 31.5% and 26% with the hydrogen pretreatment at 300 °C and 400 °C respectively. At 300 °C, sintering of Co does not occur either on surface or inside the CNTs channels. However, Co sinters on the surface of CNTs while the Co inside channels resists sintering at 400 °C [232]. A micro-channel reactor system is formed based on aligned CNTs with CoRe/Al₂O₃ integrated inside a micro-channel of CNTs. This catalyst displays an improvement of Fischer-Tropsch activity four times higher than those with similar catalyst system yet without CNTs arrays [250]. For Fischer-Tropsch synthesis, the activity and selectivity toward C₅⁺ of Fe/CNT catalysts are much higher than Co/CNT, with Fe/CNT showing selectivity values of 40 to 45% while the Co/CNT showing 10 to 20% [251]. When iron

is encapsulated within CNTs, the Fischer-Tropsch activity is notably improved and the yield toward C₅+ obtained over the confined iron is twice that of the iron particle on CNTs surface. The reducibility of the confined iron catalyst is remarkably enhanced relative to iron on CNTs surface. Fischer-Tropsch reaction expedites the formation of iron carbide species with much higher catalytic activity whereas cobalt cannot form carbide. And the trapping of reaction intermediates in CNTs channels could prolong the reaction time contacting catalysts, leading to the growth of heavier hydrocarbons [252]. CNTs have been used to promote the catalytic performance of Cu–ZnO–Al₂O₃ catalysts for methanol synthesis. This catalyst, containing 10% to 15% CNTs, gives rise to a significant increase in the formation rate of methanol when compared to Cu–ZnO–Al₂O₃ systems without CNTs. The role of CNTs can be attributed to (a) the presence of CNTs allowing a considerable increase in Cu surface area and (b) the function of CNTs for hydrogen storage [242]. It is proposed that high concentration of hydrogen species on CNT-based catalyst facilitates hydrogenation reactions for higher alcohol synthesis. In CO hydrogenation reaction to form C₂-8 oxygenates over Co-Cu catalyst, an improved CO conversion value has been obtained [245]. The strong influence of CNTs on chemical states of metal nanoparticles through the interaction between CNTs support and Ni–Mo components leads to growth of the percentage of Mo⁴⁺/Mo⁵⁺ and NiO(OH), which are two types of catalytic species associated with the selectivity toward C₁–3 alcohols, as well as the apparent decrease of the percentage of Mo⁰ and Ni⁰, which are two types of catalytic species for selective generation of hydrocarbons, especially methane. Furthermore, the sp²-C sites on CNTs support can contribute to the hydrogen adsorption-activation process. These factors give rise to an increase in selectivity toward C₁–3

alcohols [244, 246]. Ni-functionalized CNTs supported Ni–Mo–K catalyst has even better catalytic performance than CNTs supported Ni–Mo–K catalyst in synthesis of C1-3 alcohols from syngas. Proper functionalization of the CNTs with nickel nanoparticles could increase the hydrogen absorbance capability of CNTs, further enhancing their promoter action [243].

CNTs supported catalysts have been investigated for catalytic dehydrogenation reactions, a range of valuable reactions in chemical industries and hydrogen fuel production. Compared to carbon black, activated carbon, graphite, and carbon nanofibres, CNTs supported Platinum exhibits the highest yield toward H₂ in the microwave-assisted dehydrogenation reaction of decalin, due to the relatively small platinum nanoparticles formed on CNTs surface as well as the highest temperature attained by the system during the microwave-assisted dehydrogenation process [253]. Acid treated CNTs possess a number of defects and oxygen-containing groups and the defects have been proved to be responsible for the improvement of platinum catalytic activity in the ammonia borane hydrolysis instead of oxygen-containing groups. After acid treatment followed by an inert atmospheric heat treatment of CNTs, the defect-rich CNTs supported platinum has high catalytic activities, with an exceptional H₂ generation turnover frequency as high as 567 molH₂ molPt⁻¹ min⁻¹ at 30 °C, much higher than those of alumina, ceria or activated carbons supported platinum [254]. Because of the electronic properties of CNTs as well as its less acid sites, Co/CNT has higher selectivity to cyclohexanone than Co/activated carbon in cyclohexanol dehydrogenation reaction. Appropriate addition of K could improve the catalytic performance, due to the electronic promotion effect, which is also stronger for Co–K/CNT than Co–K/activated carbon [255]. Nitrogen doping CNTs can

efficiently improve the catalytic behavior of CNTs. The N-doped CNT catalysts with appropriate amount of nitrogen are quite stable and active for the oxidative dehydrogenation of propane. The graphitic nitrogen plays a crucial role in elevating the catalytic activity via diminishing the activation energy and accelerating the oxygen activation [199]. Surface curvature enhances the CNTs electronic properties and leads to electron and charge transfer from CNTs to nanoparticles, which promotes catalytic activity. Oxygen-containing functional groups on CNTs introduce active sites where dehydrogenation of reactants occurs, leading to metal-support synergetic effect. Metal nanoparticles supported on N-doped CNTs have superior catalytic performance than those supported on pristine CNTs, due to the enhanced electron density, basicity and the existence of CNT-N+:H sites. The accelerated electron transfer from N-doped CNTs toward metal nanoparticles motives the metal activation and the formation of chemical bonds between metal nanoparticles and support [205].

CNTs-based catalysts have been extensively investigated for oxidation reactions. Pt [256-258], Ru [258, 259], and Cu [258, 260] supported on CNTs have been employed to catalyze the oxidation of aniline or phenol [261]. When the oxidation reaction undergoes at a high temperature, Co/CNT catalyst possesses better conversion than Co/activated carbon for CO oxidation at 250 °C, due to the high thermal stability of nanotubes [262]. CNTs have also been applied to support Cu–Zn bimetallic catalyst for partial oxidation of methanol at 260 °C to produce hydrogen [263]. The CNTs-induced growth of vanadium oxide nanorod-CNTs composites is catalytically active for n-butane partial oxidation toward maleic anhydride [264]. Surface-functionalization of CNTs can highly promote the catalytic performance of CNTs supported catalysts for oxidation reactions.

Homogeneously dispersed manganese oxide on CNTs supported palladium catalyst was developed via impregnation method. The coupling of the manganese oxide modified CNTs with palladium nanoparticles is a promising process to improve the catalytic performance in aerobic selective oxidation of benzyl alcohol. The roles of manganese oxides particles are implied in three respects: (a) favoring the interfacial electron transfer between Pd and manganese oxide; (b) promoting the oxygen activation via transferring lattice oxygen to the active sites. And the oxygen vacancies in manganese oxide were quickly replenished with molecular oxygen; (c) manganese oxide plays a significant role in stabilizing palladium ionic species, and preventing agglomeration of metal nanoparticles [118]. CeO₂ functionalized CNTs supported Pt catalyst possesses superior catalytic performance including both catalytic activity and selectivity for CO oxidation at low temperatures (CO conversion 80% at 350 K), compared to Pt/CNT and Pt/AC. The favorable roles of the CeO₂, as a reducible oxide, has been implied as the result of a reaction mechanism alteration from Langmuir–Hinshelwood mechanism (CO and O₂ molecules compete for active sites on noble metal surface) to a free-competition dual-site mechanism (CeO₂ favors the increasing of oxygen supply on the metal–support interface, and therefore promotes the CO oxidation) as suggested by Mars et al [265, 266]. There are other applications of inorganic nanoparticles as functionalities on catalytic support, where the roles of the functionalities includes to stabilize active phase, modify the electronic properties of the catalysis, enhance metal-support interactions, alter the surface acid-base properties and so forth in order to promote the performance of the correspondent catalysts [267-269]. In addition, organic surface functional groups are promising promoters for CNTs based catalysts as well. Sulfur-functionalized CNTs

supported Pt displays excellent catalytic performance in methanol oxidation, enabling high dispersion of Pt nanoparticles smaller than 3 nm without deteriorating the intrinsic conductivity of CNTs [270]. The 3-aminopropyltriethoxysilane has been reported as superior surface functional groups for CNTs supported palladium catalyzed solvent free oxidation of benzyl alcohol using O₂ as the oxidant, along with the high values of catalytic activity and benzaldehyde selectivity, ascribed to the proper enhancement of surface basicity, electron density, metal-support interactions and diminished particle size and size distribution of the palladium nanoparticles as well [150].

The usage of Ru/C catalysts for ammonia synthesis is an alternative to replace conventional iron-based catalysts conducted at high temperature and under high pressure. Nevertheless, plenty of studies demonstrated the Ru/activated carbon deactivation after long reaction duration, as a result of metal sintering, leaching, as well as the support methanation effect. Since CNTs have higher thermal stability than activated carbon, Ru/CNT was investigated [271-274]. Promising activities have been observed when using Ru-K/MWNT and Ru-K/MgO-CNT catalysts [271, 272]. The high-extent graphitization of the CNTs support is adopted to explain the resistance against the methanation effect of carbonaceous supports. The ammonia decomposition to produce H₂ without CO for fuel cells has attracted great attention as it is more economical than methanol decomposition as hydrogen source. Ru is also employed, and the application of CNTs to support the metal has been studied [275-280]. The order of catalytic activities is Ru/CNT>Ru/MgO>Ru/TiO₂>Ru/Al₂O₃>Ru/ZrO₂>Ru/AC [278]. Highly dispersed catalysts with Ru particle size around 2 nm have high catalytic activity for NH₃ decomposition owing to the basic and conductive CNTs as the catalytic support. Using

various basic surface functionalities can enhance the conductivity and catalytic activities ranged in the order of RuK>RuNa>RuLi>RuCe>RuBa>RuLa>RuCa>Ru [276]. Employing conductive support enables electron transfer from functionalities or support to Ru, facilitating the recombination and desorption of nitrogen atoms [278], which is the rate-determining step. Accordingly, the nitrogen-doped CNTs support leads to excellent Ru dispersion and the increased conductivity also contributes to the improved catalytic performance in ammonia decomposition reaction [281]. On the other hand, the catalytic performance can be improved by the removal of electron-withdrawing species [278]. In addition, the impact of graphitic structure of carbonaceous supports on the catalytic activity ranged in the order of Ru/graphitic carbon>Ru/CNT>Ru/carbon black>Ru/AC [280]. These results have indicated the significance of the conductive carbonaceous graphitic structure which facilitates metal-support electron transfer.

One vital problem associated with the carbon nanotubes synthesis over conventional catalysts on the industrial scale is the purification step to eliminate the catalysts and supports from the final product. The use of CNT supported catalysts to produce CNTs has been explored in order to avoid the costly purification step. Besides noble metal catalysts such as Pd or Os which are seldom used in CNTs synthesis [282], iron, cobalt and nickel are three most frequently used catalysts supported on CNTs for synthesis of CNTs [283-287]. Fe, Co and Ni supported on SWNTs respectively for acetylene decomposition to grow MWNTs via chemical vapor deposition method have been investigated [283]. The Fe-Mo catalyst supported on CNTs is catalytically active for the high conversion of methane decomposition to produce well-grown CNTs of highly ordered morphology [284]. Acid pretreatment of CNTs support facilitates higher metal dispersion of Ni-Al

catalysts, higher specific surface area and hence enhanced catalytic activity for propane decomposition to synthesize CNTs [285]. Nitric acid treatment of CNTs as catalytic support plays a crucial role for nickel deposition and has a positive influence on the performance of nickel catalyst for CNTs synthesis [286]. Besides metallic nitrates as metal precursors, ferrocene is also employed for iron catalyst supported on CNTs through in situ pyrolysis process. This catalyst demonstrates feasibility using a floating catalytically chemical vapor deposition method for CNTs synthesis in nano-agglomerate fluidized bed reactor [287].

2.5 Reaction parameters in selective oxidation of benzyl alcohol and glycerol

The reaction parameters including temperature, gas flow rate, amount of reactants, and solvents can significantly affect the catalytic behavior. The preferential reaction parameters are useful in determining the structure and properties of the catalyst. For example, at high temperature, stability and resistance against poison might be the most important quality for a superior catalyst. For reactions taking place in liquid phase, engineering on the structure of catalysts is usually inevitable in order to minimize the mass transport resistance. For example, CNTs based catalysts are suitable for reactions taking place in liquid phase since they can reduce the effect of mass diffusion effect [150]. Structure of substrates may also influence the selectivity and activity over heterogeneous catalysts by means of electronic and inductive effects of substrates and the adsorption mode of substrates [118]. The nano-ligands of MnO_x for Pd particles could facilitate the electron transfer at the Pd- MnO_x interfacial region, which alters the physiochemical properties of the catalyst because of the perturbation of electron structure of the active sites as well as promote the oxygen activation by conveying lattice oxygen to Pd active

site. During the oxidation reaction, oxygen vacancies inside MnO_x clusters are created and replenished with molecular oxygen because of the highly reducible nature of transition metal oxide [118].

2.6 Role of organosilanes functional groups on carbon support for catalysis

Surface-functionalization with organosilanes is an approach to control the surface chemistry of catalyst support and subsequently fine-tune the metal dispersions and metal-support interactions of catalysts. Chen et al. suggested that certain surface organic groups can selectively modify the surface chemistry and hydrophobicity of silica support, thus controlled the size of metal nanoparticles, and dramatically elevated the palladium catalytic performance for benzyl alcohol oxidation [288]. La Parola et al. reported the mercaptopropyl-functionalization of mesoporous silica with enhanced dispersion of metal nanoparticles and metal-support interactions, which further promoted the catalytic activity in the hydrodesulphurization [289]. Organosilanes are superior surface functionalities not only for conventional groups but also for carbon supports. Yan et al synthesized the organosilanes functionalized CNTs supported Pd catalyst for aerobic selective oxidation of benzyl alcohol with high catalytic activity and selectivity [150]. The immobilized functional groups (e.g. $-\text{NH}_2$ and $-\text{SH}$) in organosilanes molecules anchor and stabilize metal nanoparticles. The localized basicity on surface-functionalized support enhanced the activation of benzyl alcohol in aerobic dehydrogenation, reduced the extent of side reactions, and accelerated desorption of intermediate products [290]. Moreover, the surface functional groups may contribute to the variation in the electron density and conductivity of carbon nanotube (CNT) supports [138]. Moreover, the well-dispersed silane-assisted Pt and Pt-Co alloy deposition on CNTs exhibit good

electrochemical catalytic behavior as cathodes in a proton exchange membrane fuel cell [153]. CNTs surface functionalization with silica layers via the hydrolysis of 3-aminopropyltriethoxysilane and tetraethoxysilane improves the durability of Ru/CNT catalyst during the repeated hexane hydrogenation reaction [225].

2.7 Role of rare earth oxides surface functionalities on carbon support for catalysis

Rare earth elements have demonstrated a broad range of applications in catalysis. Rare earth oxides-based heterogeneous catalysts have been applied in various organic chemistry reactions and rare earth oxides also attract various curiosities as a structural and electronic promoter to improve the catalyst performance of numerous catalysts over numerous supports [291-296]. Rare earth oxides also demonstrate superior effect as surface functionalities on carbon support for catalysis. Rare earth (La, Eu, Gd, Y, Sm and Er) modified PtRu/C catalysts have been prepared via chemical reduction and sintering methods. The addition of RE elements did not significantly change the average size and lattice parameter of PtRu/C particles, and the RE elements in catalysts were present in two states of the RE(0) and RE(III) oxide, which may have the amorphous structure. The electrochemical reaction results validated that the PtRuRE/C catalysts exhibited a higher electrocatalytic activity for methanol oxidation than PtRu/C. The CO-tolerance results of the PtRuRE/C catalysts were superior to that of PtRu/C, and the electron effect of rare earth played a vital role in the catalyst behavior of the PtRuRE/C catalysts for methanol electro-oxidation [297]. The catalytic properties of carbon supported nickel for Fischer-Tropsch reactions are significantly dependent upon the rare earth promoters via the formation of specific active centers [298].

2.8 Role of chemical treatment of carbon materials for catalytic support for catalysis

Acid treatment is commonly used to create oxygen-containing groups on carbon surface. Oxidation with nitric acid serves as a highly effective and controllable method to generate functional groups through tuning the treatment parameters such as temperature, duration and acid concentration. The creation of surface oxygen-containing groups enhances the wettability or hydrophilicity, electrochemical capacitance and specific surface area of carbonaceous materials [2]. Treatment of carbon with sulfuric acid creates sulfonic acid groups grafted on carbon surface, which can be employed as recyclable solid acid catalyst for rearrangement, esterification and condensation reactions [299]. Mixture of carbon materials and KOH was heated to form micro-pores by framework etching. During this process, carbon was oxidized to carbonate related ions, increasing the BET surface area and pore volume [300]. Heating carbon materials at high temperature with the presence of carbon dioxide also etches carbon surface and creates more pore volume and larger surface area since the carbon can be oxidized by CO₂ to generate CO [301, 302]. Carbon spheres simply refluxing with alkali aqueous solution at room temperature generates deprotonated –COO[–] groups since alkali can induce the hydrolysis of lactone and deprotonate the carboxyl groups [303] and thus further increase the surface hydrophilicity and adsorption capacitance for metallic ion species which can be used for catalysis.

This work has been published on Chemical Society Reviews (Yan et al., Chemical Society Reviews, 44 (2015) 3295-3346), adopted in this chapter with the permission of Royal Society of Chemistry.

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Chapter 3 Techniques of Characterization, Synthesis, and Catalytic Reactions

Characterization techniques are necessary to conceal the physiochemical properties of catalysts which determine the catalytic performance. With the help of advanced characterization methodologies, the properties of catalysts can be studied on molecular or atomic level, and therefore the catalysts can be designed accordingly. To properly take advantage of the characterization technologies, it is essential to establish a comprehensive understanding of the fundamental concepts associated with these techniques which will be briefly introduced in this chapter and the synthesis methodologies of the catalysts together with the synthetic process of support materials 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 °) are not resulted from uniform atom arrangement in crystals leading to high angle signals (10-80 °), but from the highly ordered pore walls [1]. In this PhD work, XRD characterization was performed on a Bruker AXS D8 XRD diffractometer (Cu K α , $\lambda=1.542\text{\AA}$, 40 KV, 30 mA) with the step width of 0.02° (2 θ).

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 (0.001-10 Torr) measurements. Pore size and pore size distributions have been obtained via analyzing the desorption branch of isotherms.

Transmission electron microscope (TEM) and scanning electron microscopy (SEM) can achieve direct observations of catalyst morphologies and textures. In this thesis, SEM images were obtained by a JEOL Field Emission JSM-6700F-FESEM. Before measurements, the samples were loaded on a sample holder with adhesive carbon double-sided tape and subsequently deposited with atomic gold via sputtering. TEM was carried out on JEOL JEM-2010, at 200 KV. Prior to characterization, samples were dispersed in ethanol, dropped and dried on carbon-coated copper grids.

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 α = 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. The inductively coupled plasma (ICP) method was used to analyze the metal content. Samples were dissolved by nitrolysis via Milestone microwave laboratory system and examined by Perkin-Elmer Dual-view Optima 5300 DV ICP-OES (Optical Emission Spectrometry) system.

3.1.3 Characterization of chemical properties of catalysts

The solid-state NMR spectroscopy which is a commonly used technique to characterize functionalized silica materials has not been usually reported for analysis of functionalized CNTs. Nonetheless, high-resolution solid-state ^{13}C NMR has been well developed to monitor coals and activated carbons. Liquid state proton NMR (^1H NMR) was frequently used for detecting either soluble CNTs or insoluble CNTs in suspensions. A functionalized 2-Azaxanthone functionalized CNTs dissolved in [D₆]DMSO was monitored by ^1H NMR and the anisotropy introduced by CNTs lead to changes in characteristic signals of azaxanthyl groups compared with its precursor, implying the successful surface functionalization of CNTs with azaxanthyl groups [6]. Thiol-functionalized CNTs suspended in CDCl_3 were monitored by proton NMR in order to confirm the surface groups covalently bonded by the successful thiolation reaction [7]. Organometallic salts- functionalized CNTs was reported to be analyzed by ^1H NMR for the shifts of corresponding signals compared with the organometallic precursors, proving

the success of surface functionalization [8]. Polymer-functionalized CNTs were frequently characterized by ^1H NMR [9, 10] and ^{13}C NMR [11] for the confirmation of surface groups. ^{29}Si NMR and ^{11}B NMR were used for characterization of Si(B)CN-CNT dissolved in C_2D_6 for liquid NMR and bare Si(B)CN-CNT for solid state NMR. The presence of signals may be different between the liquid state NMR and solid state NMR of the Si in the same sample due to the change in Si magnetic environment caused by long range coupling possibly because of the B-based functional groups forming B–C or B–N chemical bonds [12]. Solid state NMR was also employed, for instance, the solid state ^{13}C magic angle spinning (MAS) NMR was employed to detect the CNTs channels enriched with benzene and without phenol since the phenol was expelled out of the CNTs channels. This approach is applicable for the substantiation of the benzene hydroxylation reaction process inside the confined CNTs channels which demonstrate its feasibility in separating products from reactants [13].

FTIR spectroscopy has been commonly used for determination of surface functional groups on CNTs as well as the CNTs based composites. To substantiate the success of surface functionalization, comparison between the spectra of functionalized and non-functionalized CNTs is expedient, according to the appearance or disappearance of characteristic signals of functional groups. For example, the characteristic absorbance bands of benzene ring and sulfonic groups emerged on the FTIR spectra after surface sulfonation of CNTs [14]. 1-octadecanol treated CNTs gave rise to CH_2 stretching of long alkyl molecule at 2920 cm^{-1} and ether signals at 1473, 1458, and 1068 cm^{-1} formed from 1-octadecanol reacted with carboxylic groups [15]. Surface functionalization of CNTs with polymers such as polyaniline generates FTIR absorbance bands similar to the pure

polyaniline [16]. Phenol electro-oxidation method can functionalize CNTs with hydroquinone surface groups. Whereas the IR spectra bands were similar to the phenol data and it is hardly to decide whether it is phenol or hydroquinone functionalized on the CNTs surface [17]. For composite such as the poly(methyl methacrylate) (PMMA) functionalized CNTs, it was also characterized by FTIR. The spectra demonstrated a peak at 1132 cm^{-1} , attributed to the -O- bond inside the PMMA molecule. Additionally, the peak at 1384 cm^{-1} , ascribed to the -OH bond, approves the presence of PMMA [18]. In another case of CNTs based composite, the FTIR spectra of poly(2,6-dimethyl-1,4-phenylene oxide (PPO) functionalized CNTs composite exhibited the signals of phenyl and Ar-O-Ar groups indicating the presence of PPO [19]. As for metal particles (i.e., Au) functionalized CNTs, the FTIR spectra displayed the characteristic peaks of hydroxyl, carboxyl, acyl chloride and amide groups resulted from the MWNT-COCl connected with the cysteine capped gold nanoparticles [20]. FTIR is a quite convenient approach and widely applied for detection of surface groups, polymers and chemical bonds. However, in cases of carbonaceous materials, spectra are often of inadequate quality with low signal-to-noise ratios and different background features. This is mainly because of its strong electronic adsorption and the light scattering effects. Therefore, in order to minimize uneven light scattering, the smallest possible particle size of samples are required. When samples are mixed with KBr and pressed into pellets, the ion exchange with KBr should be circumvented. There are techniques to improve the spectra quality including attenuated total reflectance and diffuse reflectance methods [21]. Assignment regions of several commonly known functional groups detectable by FTIR technique are listed in Table 3.1.

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	[23,24]
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 (C=C=O)	2080-2200	
C-H stretch	2600-3000	
C-N stretch	1060-1250	
Aromatic C=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	[6]
Amide C=O	1650	
S-H	2200	[26]
COOH	1025, 1182, 1727, 3428	
C=N	1570, 1639	

Raman spectroscopy is a complement to FTIR since some vibrations not detectable by IR can be active in Raman. Most of the Raman characterizations of carbon materials are aimed to determine the proportion of graphitic and disordered carbon, according to the G and D bands centered at or nearby 1590 and 1330 cm⁻¹, respectively [16, 19, 27]. In a typical spectra, there are three main characteristic bands (D, D', and G modes) in the region between 1000 and 2000 cm⁻¹, and the overtone and combination bands in the region from 2400 to 3400 cm⁻¹ (G' = 2D). The G mode (E_{2g} symmetry) is ascribed to the sp² graphitic structure, whereas the D and D' (A_{1g} symmetry) modes are caused by the

Raman double resonant scattering from nonzero-center phonon modes which are originated from amorphous disorder and defects within the carbon lattice. Consequently, the intensity ratio of I_D/I_G is frequently used as a measurement of the crystallite and amorphous sites density [27]. The typical radial breathing modes (RBM) usually range from 100 to 350 cm^{-1} . It is associated with the radial expansion-contraction of the CNTs. Therefore, the frequency of RBM largely depends upon the diameter of nanotube. The larger the diameter, the lower the frequency will be [28, 29].

Accessible surface acid or basic sites are amenable to characterization by chemical titration and acid-base depletion. The oxygen-containing groups on CNTs, usually the protic functional groups, such as ketone, phenol, lactone, lactol, carboxylic acid, and carboxylic anhydride are neutralized with various base solutions such as NaOC_2H_5 , NaOH , Na_2CO_3 , and NaHCO_3 , followed by the back-titrating the bases with typical strong acid. Since the acid dissociation constants (pK_a) of these protic functional groups differ from each other by several orders of magnitude, titration with bases can help determine the concentration of surface acidic groups with the reference of the specific pK_a or pK_b data of the corresponding acid or base from titration data [23]. Mass titration or electrophoresis is also able to determine the surface charges and isoelectric points of carbon materials [30]. Calorimetric measurements of heats produced from the reaction can complement this information [31]. Titration is usually accompanied with other characterization techniques, such as FTIR. In addition, carboxylic groups can also be assured by chemical-detection methods such as esterification or formation of acyl chlorides using thionyl chloride [30].

Surface functional groups that release gas-phase products via decomposing at specific temperatures can be characterized by TPD techniques, for instance, the differential scanning calorimeter and a thermo-gravimetric analyzer (DSC-TGA) combined with a mass spectrometer (MS) [31]. Oxygen-containing groups decompose within a certain range of temperatures to form CO, CO₂ or H₂O. Accordingly, the relative concentrations of oxygen can be calculated through deconvolution of these gases [31]. The decomposition activation energies of surface groups can be calculated from the decomposition rates [32]. TPR is aimed to study the reactivity of surface groups upon sample heating with the similar process of TPD under a hydrogen atmosphere [33]. Reduction reaction occurs on surface complexes which desorb afterward, leaving active carbon sites exposure to hydrogen for further reaction. It is feasible to determine the identity and amount of surface functional groups from TPR and TPD data [34].

3.1.4 Characterization of electronic properties of catalysts

In spite of the traditional characterization techniques, electrochemistry tests including cyclic voltammetry (CV) and CO stripping have been employed to study the electrochemical properties of catalyst support and catalytically active metal nanoparticles respectively. These methods are frequently used to examine electro-catalysts since they are surface electro-chemically sensitive characterization methods [35]. In this study, the electrochemical results were interrelated with the physiochemical properties of catalysts and the catalytic performances. CV and CO stripping can be set as potential sweeping methods where the current is recorded when potential is linearly changed with time within a certain potential range. For supported metallic catalysts, the CV signals are remarkably sensitive to redox reactions of surface species. These signals contain

information of chemical environment and chemical state of metallic active centers. A typical CV spectrum of highly porous Pt electrode in H₂SO₄ aqueous solution is shown in Figure 3.1. The Pt electrochemical active surface (EAS) area can be calculated according to the amount of exchanged electrons in the process of electrochemical adsorption (Q') and desorption (Q'') of hydrogen over active sites by using Equation 3.1 [36]:

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

where the [Pt] is the mg/cm² of Pt loading on working electrode; QH is the mean value of Q' and Q'' (mC/cm²); and 0.21 is the charge required for oxidizing 1 atom layer of hydrogen on unit Pt (unit: mC/cm²).

Figure 3.1 CV profile of highly porous Pt electrode in H₂SO₄. Q' and Q'' are the amount of exchanged electrons during the electrochemical adsorption and desorption of hydrogen on Pt surface respectively. The hatching area is resulted from the double layer charges [35, 36].

In contrast, the electrochemical results originated from CV measurement are restricted when heterogeneously supported catalysts are characterized because of the low loading of metals and large background resulted from the supports. Consequently, the signals of hydrogen adsorption and desorption are hardly discerned in some cases.

Accordingly, CO stripping method was used to detect the electrochemical status of active sites and measure the EAS. In a typical experiment, CO is bubbled in the cell and adsorbed on the surface of active sites on working electrode at a low potential, then the potential sweeps like a waveform function of conventional CV. In the positively sweeping process, monolayer of CO molecules can be oxidized to CO₂ and released from the metal surface as shown in Figure 3.2. By subtracting the effect of CO free catalyst for the second scan, the onset potential and peak potential of CO stripping voltammograms and the charge exchanged during CO electro-oxidization (QCO) can be measured (see Figure 3.2). The values of CO oxidation onset and peak potentials can be employed to evaluate the oxidation capability of metallic active sites. Lower onset and peak potentials imply the easier occurrence of CO oxidation reaction [36]. Analogous to CV measurement, the EAS area can also be calculated according to the QCO value by Equation 3.2 [36] :

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

in which [Pt] is the mg/cm² Pt loading on working electrode; QCO is the exchanged charge (mC/cm²) of CO oxidization; 0.484 means the required charge for oxidizing 1 atom layer of CO on unit Pt surface (unit= mC/cm²).

Figure 3.2 Scheme of CO stripping on a Pt nanoparticle and the CO stripping voltammograms of Pt supported on CNTs in KOH aqueous solution. Q_{CO} is the required exchanged charge during CO oxidation.

In this experiment, the CV and CO stripping voltammetry were performed in 1.0 M KOH aqueous solution at the step width of 50 mV s^{-1} using Princeton Applied Research, VersaSTAT 3 Potentiostat/Galvanostat. Catalyst ink was prepared by dispersing 2 mg of catalyst into 3 mL of 0.025 wt.% Nafion in ethanol solution ultrasonically. The working electrode was prepared by dropping 30 μL of ink onto glassy carbon electrode within carbon area. Hg/HgO (1.0 M KOH) electrode and Pt foil were employed as reference and counter electrodes respectively. Potential range of CV measurement was set between -0.8 and 0.3 V. CO stripping was carried out in the following procedures: after purging nitrogen into KOH aqueous solution for 20 min, CO was purged for another 15 min to generate CO layer on the catalyst surfaces meanwhile the potential was kept at -0.8 V. Potential of CO stripping voltammetry was also ranged between -0.8 and 0.3 V.

3.2 Synthesis methodologies

3.2.1 Materials

CNT (>95%, Cnano), (3-aminopropyl) triethoxysilane (APS, $\geq$ 98%, Sigma- Aldrich), hexamethyldisilazane (HMDS, Sigma), [3-(2-aminoethylamino) propyl] trimethoxysilane (ATMS, 97%, Aldrich), concentrated nitric acid (69%, Sigma-Aldrich), PdCl₂ (>99%, Aldrich), lanthanum(III) nitrate hexahydrate (>99.999%, Aldrich), samarium(III) nitrate hexahydrate (>99.9%, Aldrich), cerium(III) nitrate hexahydrate (99%, Fluka), gadolinium(III) nitrate hexahydrate (>99.9%, Aldrich), erbium(III) nitrate pentahydrate (99.9%, Aldrich), ytterbium(III) nitrate pentahydrate (>99.9%, Aldrich), alpha-D(+)-glucose (Sigma, 99.5%, anhydrous), chloric acid HCl (36-38 wt.%), potassium hydroxide KOH (90%, Sigma-Aldrich), sodium hydroxide NaOH (>98%, Sigma-Aldrich), sodium borohydride NaBH₄ (>99%, Fluka), 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), glycerol (>99%, Sigma), acetaldehyde (>99.5%, Fluka), Cinnamaldehyde (>95%, Aldrich), 1,3-dihydroxyacetone dimer (DHA, 98%), glyceric acid (GLYA, 40 wt.% aqueous solution), glycolic acid (GLYCA, 98%), glyceraldehyde (GLYHD, 95%), hydroxypyruvic acid (HPYA, 95%), oxalic acid (OXA, 98%), tartronic acid (TARAC, 95%), mesoxalic acid (MOXA, 98%) and glyoxylic acid (GLYOA, 98%), ethyl acetate (EA, >99.8%, Sigma-Aldrich)

3.2.2 Preparation of Pd supported on CNTs by ion adsorption reduction method

Palladium nanoparticles supported on surface-functionalized CNT were prepared by adsorption-reduction method [37]. Mixture of 375.9 μ L of 0.05M PdCl₂ aqueous solution and 0.2 g of CNTs was suspended in 20 mL of deionized water, followed by stirring for 5 h at 80 °C. The resulting powders were filtered, washed with deionized water, and dried

at 80 °C overnight. The catalysts were reduced at 400 °C under H₂ flow of 20 mL min⁻¹ for 2 h. This ion adsorption reduction method was used for stronger metal-support interaction in order to inhibit leaching of metallic active phase during the catalytic reactions, in contrast to traditional wet impregnation methods.

3.2.3 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. [38].

3.2.4 Preparation of CNTs functionalized with organosilanes groups

Abundant surface functional groups were created during the pretreatment with nitric acid, which served as anchoring sites for the further post-synthesis grafting of organosilane functionalities. Organosilanes, i.e., (3-aminopropyl) triethoxysilane (APS, ≥98%, Sigma- Aldrich), hexamethyldisilazane (HMDS, Sigma), [3-(2-aminoethylamino) propyl] trimethoxysilane (ATMS, 97%, Aldrich) were linked onto CNT surfaces via a post-synthesis grafting method. APS-functionalized CNT was displayed as an example for a typical preparation procedure. 1.0 g of CNT was suspended in 30 mL of toluene and refluxed for 12 h at 110 °C under nitrogen flow (50 mL min⁻¹), followed by adding 2.4

mmol of APS (or a certain amount of other silane modifiers) and stirring continuously for 5 h. After filtering the mixture, the resulting powder was washed with toluene, and dried at 80 °C. The samples were correspondingly denoted as APS-CNT, ATMS-CNT and HMDS-CNT.

Palladium nanoparticles supported on surface-functionalized CNT were prepared by adsorption-reduction method [37]. Mixture of 375.9 μL of 0.05M PdCl_2 aqueous solution and 0.2 g of surface-functionalized CNT, e.g., APS-CNT, were suspended in 20 mL of deionized water, followed by stirring for 5 h at 80 °C. The resulting powders were filtered, washed with deionized water, and dried at 80 °C overnight. The catalysts were reduced at 400 °C under H_2 flow of 20 mL min^{-1} for 2 h and correspondingly denoted as 1Pd/APS-CNT where 1 indicates the 1 wt.% of Pd loading.

3.2.5 Preparation of CNTs functionalized with rare earth oxides

CNTs were surface-functionalized using rare earth nitrates $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\text{Ln}=\text{La}$, Ce, Sm, Gd, Er, Yb) following these steps: 0.25 g of pretreated CNTs powder and a certain amount of each rare earth nitrate $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were suspended in 20 mL of deionized water, where the content of rare earth element was controlled at 5 wt.% respectively for each mixture. After stirring for 4h and aging for 12 h, each mixture was evaporated in 80 °C water bath and dried at 80 °C overnight, followed by calcination in tube furnace at 400 °C for 4 h under nitrogen flow in order to generate LnO_x/CNT from their precursors.

Adsorption-reduction method reported by Chi et al. [37] was employed to deposit palladium nanoparticles onto LnO_x/CNT functionalized support: 379.7 μL of 0.05 M PdCl_2 aqueous solution was added to 0.2 g of LnO_x/CNT functionalized support and the

mixture, suspended in 20 mL of deionized water, followed by refluxing at 80 °C for 5 h. Each suspension was filtered, washed and dried overnight. After reduction in hydrogen flow at 400 °C for 2 h, the catalysts, denoted as Pd/LnO_x-CNT (Ln=La, Ce, Sm, Gd, Er, Yb), were obtained.

3.2.6 Preparation of carbon nanospheres

The preparation method of carbon nanospheres refers to the hydrothermal approach reported in the literatures [39, 40]. 3.6 g of alpha-D(+)-glucose (Sigma, 99.5%, anhydrous) was dissolved in ultrapure water to make 40 mL of 0.5 M aqueous solution via ultrasonication for 30 min before being placed into a 45 mL Teflon-lined hydrothermal autoclave and maintained at 160 °C for 12 h. Then the as-synthesized carbon nanospheres were rinsed with ultrapure water and ethanol for at least three times through centrifugations followed by drying at 60 °C overnight.

3.2.7 Surface functionalization of carbon nanospheres

The native CNS was then surface functionalized via immersing into sodium hydroxide aqueous solutions. 0.24 g of dry CNS powder was dispersed in 200 mL of sodium hydroxide solution of specific concentration. The suspension was vigorously stirred at 600 rpm at room temperature for 1 h, and then was collected via filtration and rinsed with 1 L of deionized water to get rid of the residual alkali until the pH of the filtrate was almost neutral. The activated CNS was dried at 60 °C for 12 h followed by grinding into fine powders. The influence of sodium hydroxide concentration has been investigated. 0.1 M, 0.3 M, 0.5 M, 0.7 M, 1 M, 3 M and 5 M of sodium hydroxide solutions activated CNS was named as CNS-0.1OH, CNS-0.3OH, CNS-0.5OH, CNS-

0.7OH, CNS-1OH, CNS-3OH and CNS-5OH respectively. The CNS sample without treatment was denoted as CNS.

3.2.8 Immobilization of Pd nanoparticles onto the functionalized carbon supports

Palladium nanoparticles supported on CNS or functionalized CNS (CNS-0.1OH, CNS-0.3OH, CNS-0.5OH, CNS-0.7OH) were synthesized by adsorption-reduction method [41]. 767.1 μL of 0.05 M PdCl_2 aqueous solution and 0.2 g of CNS or functionalized CNS were suspended in 20 mL of deionized water, and subsequently stirred at room temperature for 2 h. The palladium ions were reduced by addition of excessive 1 M NaBH_4 under the protection of nitrogen and stirring overnight. Then the suspension was centrifuged, rinsed with ultrapure water and dried in a vacuum drying oven.

3.3 Catalytic reactions

3.3.1 Selective oxidation of benzyl alcohol

The catalytic reaction employed solvent-free oxidation of benzyl alcohol with molecular oxygen in a bath-type reactor under the atmospheric pressure. 50 mmol of benzyl alcohol (5.174mL) was added into a three-necked glass flask pre-charged with 0.01 g of catalyst (benzyl alcohol/Pd=500 mol/g). The flask was immersed in a 160 $^{\circ}\text{C}$ of silicone oil bath with the oxygen flow rate of 20 mL min^{-1} 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, turnover frequency (TOF) and quasi-turnover frequency (qTOF) are as follows [43, 44], where the electro-active surface area was measured by CO stripping voltammetry [44]:

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

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

$$\text{TOF (h}^{-1}\text{)} = \frac{\text{Moles of reactant converted}}{\text{Moles of Pd} \times \text{reaction time (h)}}$$

$$\text{qTOF (h}^{-1}\text{)} = \frac{\text{Moles of reactant converted}}{\text{Moles of Pd} \times \text{dispersion} \times \text{reaction time (h)}}$$

$$\text{dispersion} = \frac{\text{Electroactive surface area}}{(1/\text{Atomic weight of Pd}) \times (N_A \times 4\pi r_{Pd}^2)}$$

3.3.2 Selective oxidation of glycerol

Selective oxidation of glycerol has been carried out in a three-necked flask with a bubbled gas supplied system, condenser, magnetic stirring and thermocouple. 20 mL of 10 wt.% glycerol solution and 50 mg of catalyst were added to the flask. Oxygen was purged into the liquid at 150 mL/min by mass flow controller. Catalyst was filtered off and liquid phase was charged into a 50 mL flask and monitored by a high performance liquid chromatography (Agilent 1260 Infinity HPLC) armed with UV-VIS detector (G1314B variable wavelength detector 1260 VWD VL), refractive index detector (G1362A 1260 RID), thermostatted column compartment (G1316A TCC), G1322A standard degasser and Alltech OA-1000 Organic Acid HPLC Column was used with the diluted 4 mmol/L sulfuric acid as the eluent. Before performing the HPLC analysis of reaction products, each of the glycerol (>99.0%), 1,3-dihydroxyacetone dimer (DHA, 98%), glyceric acid (GLYA, 40 wt.% aqueous solution), glycolic acid (GLYCA, 98%),

glyceraldehyde (GLYHD, 95%), hydroxypyruvic acid (HPYA, 95%), oxalic acid (OXA, 98%), tartronic acid (TARAC, 95%), mesoxalic acid (MOXA, 98%) and glyoxylic acid (GLYOA, 98%) was run individually for calibration of the standard retention time of each possible product.

3.3.3 Aldol condensation reaction to produce cinnamaldehyde

Synthesis of cinnamaldehyde was conducted according to the following process. 1 mL of benzaldehyde was added with 1 mL of acetaldehyde, 0.1 g of CNS or functionalized CNS (CNS-1OH, CNS-3OH and CNS-5OH), 10 mL of deionized water together with 5 mL of ethanol. The aldol condensation reaction was carried out in a Teflon-lined sealed steel reactor stirring by a motor stirrer at a certain temperature (20 °C, 25 °C, 30 °C, 35 °C and 40 °C) for 5 h under the protection of nitrogen gas flow. After the reaction, the suspension was centrifuged and the organic phase was analyzed by the Agilent gas chromatography installed with a HP-5 column. The control experiment was also performed using 20 mL of NaOH aqueous solutions of certain concentrations (0.01 M, 0.05 M, 0.07 M, 0.1 M, 0.2 M, 0.5 M and 0.7 M respectively denoted as NaOH-0.01M, NaOH-0.05M, NaOH-0.07M, NaOH-0.1M, NaOH-0.2M, NaOH-0.5M and NaOH-0.7M) instead of the mixture of CNS and deionized water.

List of abbreviations

CALD	Cinnamaldehyde
CD	Circular Dichroism
CNTs	Multi-Walled Carbon Nanotubes
CO Stripping	Carbon Monoxide Stripping
CV	Cyclic Voltammetry
DHA	1,3-dihydroxyacetone
DMSO	Dimethyl Sulfoxide
EA	Ethyl Acetate
EAS	Electrochemical Active Surface
EtOH	Ethanol
FID	Flame Ionization Detector
FTIR	Fourier Transform Infrared Spectroscopy
GC-MS	Chromatography-Mass Spectrometry
GLYA	Glyceric Acid
GLYCA	Glycolic Acid
GLYOA	Glyoxylic Acid
GLYHD	Glyceraldehyde
H ₂ -TPR	Hydrogen Temperature Programmed Reduction
HPYA	Hydroxypyruvic Acid
ICP	Inductively Coupled Plasma
LCP Radiation	Left Circularly Polarized Radiation
NMR	Nuclear Magnetic Resonance

MOXA	Mesoxalic Acid
OXA	Oxalic Acid
PPO	Poly(2,6-dimethyl-1,4-phenylene oxide
PMMA	Poly(methyl methacrylate)
SEM	Scanning Electron Microscope
TARAC	Tartronic Acid
TEM	Transmission Electron Microscopy
TPD	Temperature Programmed Decomposition
UV	Ultraviolet
UV-vis	UV-visible
VCD	Vibrational Circular Dichroism
XANES	X-ray Absorption Near Edge Structure
XPS	X-ray Photoelectron Spectroscopy
XRD	X-Rays Diffraction

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Chapter 4 Palladium nanoparticles supported on organosilane-functionalized carbon nanotube for solvent-free aerobic oxidation of benzyl alcohol

Selective oxidation of alcohols to corresponding aldehydes or ketones plays a paramount role in both the laboratory and industry on account of the carbonyl versatility in organic synthesis. Extensive investigations have shed light upon the catalytic roles of noble metal nanoparticles (e.g., Pd, Pt, Au, Rh and Ru) as active sites in selective oxidation of alcohols owing to their superior catalytic performance compared to non-noble metals [1]. Since the first successful report about the Pd-catalyzed oxidation of secondary alcohol, numerous results have been presented on the Pd catalysts and their catalytic applications in alcohol oxidation. Mori et al. reported that Pd supported on hydroxyapatite (Pd/HAP) possessed a turnover frequency (TOF) of $9,800 \text{ h}^{-1}$ for 1-phenylethanol oxidation under mild conditions in the absence of solvent [2]. The zeolite-supported Pd catalysts exhibiting an extraordinarily high TOF of $18,800 \text{ h}^{-1}$ for 1-phenylethanol oxidation has been reported by Li et al. [3].

The dispersion and size distribution of metal nanoparticles make significant difference of the catalytic behavior in certain reactions such as alcohol oxidation which is generally considered as a size-dependent reaction [4]. Usually, highly dispersed metal nanoparticles with narrow size distribution exhibit excellent catalytic activity due to the specific electronic structure and high fractions of the coordination unsaturated metal atoms [5-9]. For instance, the metal particle size plays a major role in controlling catalytic activity in CO oxidation, and the activity remarkably increases when Au diameter decreases to 5 nm [10-14]. Fang et al. reported the sharp increase of TOF for benzyl alcohol dehydrogenation when the average Au particle size decreases from 4 to

2.1 nm. They suggested that the Au nanoparticles activate substrate over the low-coordination surface atoms including the edge and corner sites [5]. Chen et al. also demonstrated that small Pd nanoparticles promoted both the catalytic activity and the selectivity toward benzaldehyde in aerobic oxidation of benzyl alcohol using both experimental and multivariate statistical modeling analysis [15].

Surface property has been proven to be important to control the conversion of substrate and selectivity toward the desired product. Numerous authors suggested that dehydration of primary or secondary alcohol was catalyzed by acid sites whereas the dehydrogenation reaction to form aldehyde or ketone was catalyzed by both acid and basic sites [16-20]. Fang and co-workers reported the Au particles supported on hydrotalcite, containing both strong acidity and strong basicity surface properties, afforded the best catalytic performance among various types of supports they screened in dehydrogenation of benzyl alcohol. They speculated a mechanism with the base cleaving the O-H bond of alcohol to form alkoxide intermediate while acid sites participating with metal hydride to yield H₂ molecules [5]. Base is usually applied as a promoter into the catalyst for oxidation of alcohols [21, 22]. Wang et al. reported that surface basicity favored both conversion of benzyl alcohol and selectivity towards benzaldehyde while surface acidity promotes the conversion of benzyl alcohol at the expense of selectivity due to the formation of a large amount of byproducts, such as dibenzyl ether and hydrobenzoin [23].

CNT has attracted tremendous attention as a catalyst support material due to its high mechanical properties, electrical conductivity and thermal stability. The high accessibility of active phase remarkably eliminates mass diffusion resistance and intra-particle mass

transfer problem in reaction medium [24]. Zhou et al. reported the Pt alloyed with Fe catalysts supported on CNT for aerobic oxidation of benzyl alcohol in aqueous phase [25]. A high catalytic activity (TOF of $19,467\text{ h}^{-1}$) of Pd nanoparticles supported on manganese oxide-doped CNT has also been reported by Tan et al [26]. Surface-functionalization is an approach to control the surface chemistry of catalyst support and subsequently fine-tune the metal dispersions and metal-support interactions of catalysts. In this study, we aimed to synthesize and investigate the Pd nanoparticles supported on CNT surfaces functionalized by organosilane modifiers, especially amino-containing organosilanes groups. The as-prepared catalysts were evaluated through the aerobic oxidation of benzyl alcohol in the absence of solvent as a model reaction. Furthermore, correlation between surface chemistry, catalyst structure, electrochemical activity, and catalytic performance will be discussed in depth.

4.1 Characterization of properties of the organosilane functionalized CNT supported Pd catalysts

The surface chemistry, which is reflected from the pH in this study, has a crucial role in Pd nanoparticle sizes and size distributions and metal-support. Table 4.1 shows the pH measurements of 1Pd/CNT and surface-functionalized CNT supported catalyst. A distinct variation in pH is observed with different surface functionalities. The surface of nitric acid pretreated CNT is mildly acidic, with a pH of 6.2. APS and ATMS surface functionalized CNT correspondingly possess the increased pH to 9.1 and 9.8, respectively, indicating that amino-containing functional groups are able to enhance the basicity of CNT surfaces. HMDS-functionalized CNT shows a neutral surface as anticipated. The

pH variations further substantiate the successful functionalization with surface groups and the effective tuning of the surface basicity.

Figure 4.1 The UV-vis-NIR spectra of 1Pd/CNT, 1Pd/APS-CNT, 1Pd/ATMS-CNT and 1Pd/HMDS-CNT.

Xu et al. suggested that adsorption bands of well-isolated amino groups and hydroxyl groups cannot be resolved using FTIR due to the overlap of bending vibration between NH and hydroxyl groups in IR range [27]. Near-infrared (NIR) is able to compensate for the deficiency of FTIR in characterizing amino groups since amino groups exhibit well-resolved bands in the region between 1000 and 2500 nm, i.e., NIR region. As shown in Figure 4.1., palladium supported on hydrophilic APS- and ATMS-functionalized CNT samples demonstrate two major reflection bands: 1870 and 1900 nm indexed to the stretching and deformation vibrations for adsorbed water molecules [28], which are hardly discernible for relatively more hydrophobic 1Pd/CNT and 1Pd/HMDS-CNT

samples. The reflection band at 1998 nm is assignable to the combination of stretching (ν) and bending (δ) vibrations of the amino groups [15, 29], which cannot be observed in 1Pd/CNT catalyst due to the lack of amino groups. The reflection bands at 2170 and 2265 nm are identified to the infrared optical response of CNT when the electron charge transition from valence band to conduction band ($V_i \rightarrow C_i$) upon the photon absorption at 0.573 and 0.548 eV, respectively [30, 31]. Due to the characteristic infrared optical response of CNT support, all the samples possess evident peaks at 2170 and 2265 nm, whereas an noticeable increase of charge transfer strength occurs when functional groups (i.e., APS, ATMS and HMDS) are grafted onto the CNT surface, indicating that these functional groups can enhance the electron density on CNT surface and thus increase the number of electrons undergoing the transition from valence band to conduction band. Generally, the UV-vis-NIR spectra further verified that after surface functionalization, the CNT surfaces are indeed grafted with functional groups and these functional groups have an impact on the surface electron density of CNT support.

Raman spectroscopy was employed to characterize the CNT supports and the results are shown in Figure 4.2. The characteristic G-band, situated at 1570 cm^{-1} , is derived by the graphite-oriented Raman-active E_{2g} mode [32, 33]. Amorphous carbon-oriented D-band is centered at 1345 cm^{-1} and the second-order harmonic D'-band is indexed at 2693 cm^{-1} due to the finite size effect, lattice distortion and the structural defect [34]. The slight decrease in the G-, D- and D'-band intensities implies the less perfect structure of the nanotubes after surface-functionalization with various organosilane modifiers [33]. The ratio of G to D band peak intensity (I_G/I_D) of 1Pd/CNT, 1Pd/APS-CNT, 1Pd/ATMS-CNT and 1Pd/HMDS-CNT have been measured and the measurement results are 1.80,

1.48, 1.53 and 1.33 respectively. The decrease of IG/ID after surface-functionalization indicates the decline of purity of CNT to certain extent upon post-synthesis grafting organic groups [34].

Figure 4.2 Raman spectra of 1Pd/CNT, 1Pd/APS-CNT, 1Pd/ATMS-CNT and 1Pd/HMDS-CNT

XRD patterns and TEM images were employed to characterize the Pd catalysts supported on organosilane modified CNT surfaces. XRD patterns of catalysts with Pd loading of 1 wt.% are displayed in Figure 4.3. The XRD peaks at 26.01° and 42.80° are attributed to the (0 0 2) and (1 0 0) facets of CNT, respectively [26]. For 1Pd/CNT and 1Pd/HMDS-CNT, the diffraction peak at 40.00° is in correspondence with the (111) facet of palladium face-centered cubic (FCC) crystalline structure. The larger full width at half maximum (FWHM) value of this particular diffraction peak of 1Pd/HMDS-CNT indicates that 1Pd/HMDS-CNT possesses smaller Pd average size than 1Pd/CNT

according to Scherrer equation [35, 36]. Diffraction peaks indexed to Pd FCC structure are indiscernible for 1Pd/APS-CNT and 1Pd/ATMS-CNT, implying the highly dispersed nature of Pd nanoparticles and the particle sizes are below the detection limit of XRD.

Figure 4.3 XRD patterns of 1Pd/CNT, 1Pd/APS-CNT, 1Pd/ATMS-CNT and 1Pd/HMDS-CNT.

The higher dispersion and smaller mean size of Pd nanoparticles have been achieved after functionalizing CNT surfaces with organosilane modifiers; these results can be further verified through TEM observations and the particle size distribution histograms are illustrated in Figure 4.4. 1Pd/CNT presents a wide Pd particle size distribution scattered around 6 nm. 1Pd/APS-CNT and 1Pd/ATMS-CNT demonstrate narrow palladium nanoparticle size distributions centered at 2.1 and 3.9 nm, respectively. 1Pd/HMDS-CNT exhibits a broad size distribution with an average particle size of 6.5 nm. Upon CNT surface-functionalization with organosilanes, these groups serve as

anchoring sites for metal adsorption. Hydrophilic amino groups are highly affinitive to aqueous palladium ions and hence favor the deposition of metal precursors, which leads to highly dispersed palladium nanoparticles supported on CNT surfaces. Moreover, the basic -NH_2 and -NH- groups undergo a hydrolysis, resulting in the surfaces positively charged, which consequently shows great affinity to $\text{PdCl}_2(\text{OH})_2^{2-}$ precursors. The hydrophobic trimethyl groups shows adsorption barrier for palladium precursors and thus results in large Pd particle size with a broad size distribution. Furthermore, 1Pd/APS-CNT possesses smaller palladium nanoparticle mean size and narrower size distribution than 1Pd/ATMS-CNT. Similar results ascribed to strong interaction between Pd nanoparticles and the grafted diamino functional groups were also reported by Lee et al [37].

The Pd 3d and O 1s XPS core level spectra were investigated and deconvoluted as shown in Figure 4.5. The Pd 3d peaks were convoluted to two oxidation states due to the coexistence of Pd^0 metallic state and Pd^{2+} cationic state. The fractions of Pd^0 (Pd^0/Pd) in Pd/CNT and Pd/APS-CNT catalysts are 42.3% and 51.7% respectively, implying that the APS functional groups on CNT surface can enhance the electron density of Pd nanoparticles which is associated with the increased CNT electron density after functionalization with APS groups in agreement with the NIR measurement. The shift of Pd^{2+} 3d $_{3/2}$ and 3d $_{5/2}$ binding energy peaks toward reduced forms after APS-functionalization implies the presence of Pd in a lower oxidation state or the formation of Pd-APS complex [38]. Since APS contains C-O bonds, the apparent increase of C-O/C=O fraction of Pd/APS-CNT compared to Pd/CNT indicates the successful functionalization of APS groups onto CNT surface [26].

Figure 4.4 TEM images and particle size distribution histograms of 1 wt.% palladium supported on CNT functionalized with different functional groups: (a) 1Pd/CNT; (b) 1Pd/APS-CNT; (c) 1Pd/ATMS-CNT; (d) 1Pd/HMDS-CNT.

Figure 4.5 XPS spectra: (a) Pd 3d spectra; (b) O 1s spectra.

Cyclic voltammetry (CV) measurements were carried out to characterize their electrochemical properties as shown in Figure 4.6. With the organic groups surface-functionalized upon CNT, remarkable increase is observed in the area enclosed by CV curves, which is in correspondence with the results reported by Guo et al. that a larger amount of redox active sites or electron donor sites on CNT surfaces gave rise to a higher capacitance and a larger CV background [39], further verified the NIR results in this study. Upon CNT surface-functionalized with organic groups, i.e., APS, ATMS and HMDS, the palladium oxide (Pd-O) reduction peak shifts from -0.1 to -0.2 V. The Pd-O reduction potential depends on the metal oxide thermodynamics, reduction step kinetics

and electrochemical environment [39]. In an alkaline solution, Pd-O reduction mechanism follows the step [40]:

The decrease of Pd-O reduction potential when attaching to the functional groups on CNT surfaces indicates that surface organic functional groups covalently σ -bonded on the CNT surface can effectively hinder the Pd-O reduction. Surface-functionalization with organic groups enhances the hydrophobicity of CNT surface, which hampers the contact between water and CNT support, resulting in a difficult Pd-O reduction. Although amino-containing groups contribute a higher conductivity of CNT, which enhances the electric current in response to the electric potential applied and accelerates the electron diffusion to Pd particles, the water approachability to CNT plays a more crucial role in this particular Pd-O reduction step.

CO stripping voltammetry is carried out to measure the electrochemical active surface (EAS) areas of Pd nanoparticles. CO molecules adsorbed on Pd nanoparticles are subsequently oxidized to CO_2 at a negative onset potential followed by the positively sweeping potential on the working electrode. The commonly accepted model for CO electro-oxidation is the Langmuir–Hinshelwood mechanism, where adsorbed OH formed on the Pd surfaces by dissociative adsorption of H_2O reacts with the adsorbed CO [41].

The electrolyte KOH aqueous solution neutralizes the H^+ and promotes the reaction moving forward. Thus, CO electro-oxidation potential relies upon the kinetics,

thermodynamics and electrochemical environment of CO molecules as well as the electrochemical state of Pd. As displayed in Figure 4.7, CO electro-oxidation peak splits into multiple peaks when CNT support is surface-functionalized with organic groups. We postulated that the CNT surfaces are not homogeneous even after modifying with organic groups, i.e., Pd nanoparticles may directly in contact with organic groups, bare CNT surfaces, and bare CNT surfaces in the vicinity of organic modifiers (or vice versa). Pd nanoparticles may possess different electron densities if they are anchored at different places due to the electronic interaction between Pd nanoparticles and CNT surface substrates. Subsequently, CO molecules adsorbed on these Pd nanoparticles may show different adsorption strength, resulting in the variation of electro-oxidation potentials. The CNT surface free energy may also be different in the presence or absence of organic modifiers, which significantly impact the kinetics rate constant k_1 , k_2 and k_3 of the Langmuir–Hinshelwood mechanism. Additionally, the dynamic adsorption and desorption of CO from surface-functional groups, which possibly disturbs the CO oxidation potential on Pd surface, also contribute to the split of CO electro-oxidation peaks. The EAS areas of Pd nanoparticles have been calculated based upon the CO stripping voltammetry, with the assumption that the oxidation of a CO full monolayer adsorbed on Pd surfaces requires $420 \mu\text{C}/\text{cm}^2$ of electric charge [42]. The results in Table 4.1 show the larger electrochemical active surface area of Pd on APS and ATMS functionalized CNT support than Pd on bare CNT surfaces due to the smaller particle sizes of 1Pd/APS-CNT and 1Pd/ATMS-CNT catalysts. Pd on HMDS-functionalized CNT possesses the lowest EAS area because of the large Pd particle size.

Figure 4.6 Cyclic voltammograms of 1Pd/CNT, 1Pd/APS-CNT, 1Pd/ATMS-CNT and 1Pd/HMDS-CNT.

Figure 4.7 CO stripping voltammograms of 1Pd/CNT, 1Pd/APS-CNT, 1Pd/ATMS-CNT and 1Pd/HMDS-CNT

4.2 Effects of different organosilane functional groups

Solvent-free selective oxidation of benzyl alcohol with molecular oxygen was introduced as a probe reaction to shed light upon the effect of surface functionalization on catalytic performance of Pd nanoparticles, and the results are displayed in Table 4.1. qTOF was defined as the number of benzyl alcohol molecules converted in 1 h on one

active site determined by EAS measurements [43]. The main product is benzaldehyde and byproducts are a trace amount of toluene and benzoic acid. The catalytic activity is enhanced after functionalizing the CNT surfaces with APS and ATMS. 1Pd/APS-CNT displays the best catalytic activity with the conversion of 27.8% and the highest qTOF of $288,755 \text{ h}^{-1}$ that is 1.6 times higher than that of 1Pd/CNT. Nonetheless, the high activity is at the expense of the slightly decreased selectivity towards benzaldehyde (91.9%). 1Pd/HMDS-CNT shows the lowest catalytic activity with the conversion of 12.8% and the qTOF of $125,089 \text{ h}^{-1}$. Nevertheless, the highest selectivity towards benzaldehyde (97.6%), as well as the lowest selectivity to byproducts toluene (0.8%) and benzoic acid (1.6%) is observed.

Benzyl alcohol dehydrogenation forms benzaldehyde and co-product H_2 in the absence of O_2 . C-O bond hydrogenolysis of benzyl alcohol also occurs to form toluene when Pd is in metallic state (Pd^0) partially covered with hydrogen yielded from the benzyl alcohol dehydrogenation even in the presence of molecular oxygen [44].

Although molecular oxygen is a good acceptor for hydrogen, toluene is inevitable due to benzyl alcohol. The direct insertion of oxygen into benzyl alcohol is slow [45] and surface water is formed as a co-product, benzoic acid is formed by hydration of benzaldehyde to a geminal diol and subsequently undergoes the dehydrogenation reaction on Pd [44].

Additionally, basic sites of catalysts promote the disproportionation of benzaldehyde (i.e., the Cannizzaro reaction), forming benzoic acid and benzyl alcohol [46], which is employed to explain the effect that the -NH_2 containing APS and ATMS surface-functionalized catalysts produce more benzoic acid than 1Pd/CNT and methyl-covered 1Pd/HMDS-CNT catalysts.

Thus, the higher selectivity to benzaldehyde is ascribed to the same effect that low surface hydrogen concentration leads to diminished formation of toluene and the low surface basicity results in little extent of disproportionation of benzaldehyde to form benzoic acid.

In addition, the basic catalyst support facilitates highly dispersed and small Pd nanoparticles with narrow size distribution. Referring to the TEM results in Figure 4.2, Pd nanoparticles of 2 nm average size with a narrow size distribution on 1Pd/APS-CNT can explain the remarkably high activity of this particular catalyst, considering the vital role that Pd nanoparticle size plays in this size-dependent reaction, which is in agreement with results reported by Chen et al. [15]. The basic amino group-functionalized catalysts possess surface basicity which is suggested to facilitate the alcohol adsorption and product desorption from the Pd active sites. Although both APS and ATMS contain amino groups, diamine groups in ATMS have stronger interaction with Pd nanoparticles which hampers exposure of Pd active sites than that of monoamine in APS, hence 1Pd/APS-CNT displays more remarkable enhancement in catalytic activity. The low Pd content in 1Pd/HMDS-CNT is attributed to the adsorption barrier caused by the hydrophobic tri-methyl groups attached surface when palladium is adsorbed onto it.

According to the TEM result in Figure 4.2, this adsorption barrier also results in large Pd nanoparticle size with a broad size distribution. This particular catalyst shows the lowest benzyl alcohol conversion (12.8%), which can result from the lack of active sites owing to the low Pd content along with the large Pd particle sizes indexed in XRD and TEM. Considering the excellent yield for benzaldehyde, APS was selected as the best modifier in the following study.

Table 4.1 pH and Catalytic results of benzyl alcohol oxidation over 1Pd/CNT, 1Pd/APS-CNT, 1Pd/ATMS-CNT and 1Pd/HMDS-CNT catalysts

Catalyst	pH	Pd ^b (wt.%)	EAS ^c (m ² g ⁻¹)	Conversion (%)	Selectivity (%)			qTOF ^d (h ⁻¹)
					Benzaldehyde	Toluene	Benzoic acid	
1Pd/CNT	6.2	0.96	12.1	17.1	95.3	2.1	2.6	177,483
1Pd/APS-CNT	9.1	0.98	14.3	27.8	91.9	1.2	6.9	288,755
1Pd/ATMS-CNT	9.8	0.97	14.8	19.9	95.1	1.9	3.0	184,208
1Pd/HMDS-CNT	7.3	0.93	11.9	12.8	97.6	0.8	1.6	125,089

^a Reaction conditions: catalyst, 10mg (the amount of Pd is 1 wt.% of catalyst, 0.1mg);

benzyl alcohol, 50mmol; O₂, 20mL min⁻¹; temperatu

re, 160°C; time, 1h.

^b Metal content was obtained by ICP.

^c EAS areas were measured from CO stripping data.

^d qTOF is defined as the number of benzyl alcohol molecules converted in 1h on one active site; the number of active sites (Pd atoms exposed on the surface) is determined by EAS value [43] considering Pd content obtained from ICP, and subtracted the CNT effect (conversion ~5%).

4.3 Effects of the amount of APS functional groups

The XRD patterns of 1Pd/APS-CNT catalysts functionalized with different APS loadings are shown in Figure 4.8. There are an obvious decreasing of diffraction peak intensity at 40.00° , the Pd characteristic (111) facet, and a discernible increase of FWHM of the 40.00° peak with increasing the amount of functionalized APS groups. According to the Debye-Scherrer equation [35, 36], the average size of Pd nanoparticles decreases with the increase in FWHM and hence the increasing APS loading facilitates the Pd dispersion. The Pd characteristic diffraction peaks cannot be observed in 1Pd/2.4APS-CNT and 1Pd/3.6APS-CNT catalysts, implying the Pd nanoparticles are uniform with small sizes beyond the detection of X-ray signals. Chen et al. suggested that the specific metal-support interaction and the distribution of metal nanoparticles are dependent upon the nature of support surface chemistry [15]. After purified through the nitric acid treatment, the CNT surfaces without APS are mildly acidic and negatively charged due to the ionization of carboxyl groups, which hampers the diffusion and adsorption of $\text{PdCl}_2(\text{OH})_2^{2-}$ negatively charged precursors. After grafting the terminal APS groups, the hydrolysis of basic $-\text{NH}_2$ groups changes the surface as positively charged, showing great affinity to the negatively charged precursors. Additionally, these attached amino groups can act as anchors for the stabilization of Pd nanoparticles through covalent interactions, giving rise to highly dispersed Pd nanoparticles [15, 47]. Nonetheless, further adding APS possibly causes the oligomerization and polymerization of organosilanes which forms a cross-linked alkanolamine attached on CNT surfaces [48], making the Pd particles less finely tuned. From the TEM results shown in Figure 4.9, 1Pd/CNT possesses the largest Pd nanoparticle size with a wide distribution scattered around 6 nm.

Whereas 1Pd/2.4APS-CNT demonstrates the smallest Pd nanoparticle size with a narrow distribution centered at 2.1 nm. As the APS amount increases in the series of 0.3, 0.6, 1.2, 2.4 and 3.6 mmol per gram of CNT, Pd nanoparticle mean size turns out to be 4.5 nm, 3.9 nm, 3.1 nm, 2.1 nm and 2.3 nm respectively. Hence, the TEM observation further corroborates the XRD results that an evident decrease of Pd nanoparticle size occurs with the increase of the amount of APS surface groups.

Figure 4.8 XRD pattern of 1Pd/APS-CNT with different APS amount.

Figure 4.9 TEM graphs and Pd particle size distribution of (a) 1Pd/CNT; (b) 1Pd/0.3APS-CNT; (c) 1Pd/0.6APS-CNT; (d) 1Pd/1.2APS-CNT; (e) 1Pd/2.4APS-CNT; (f) 1Pd/3.6APS-CNT.

As mentioned earlier, the pH is able to reflect the surface chemistry, which has a crucial role in Pd nanoparticle sizes and size distributions, metal-support interaction as well as the catalytic performance in solvent-free selective oxidation of benzyl alcohol. Table 2 displays the pH measurement results of different content of APS surface-functionalized CNT supported catalysts. With the increase of APS loading, there is an increase in pH detected in the sequence of 1Pd/CNT < 1Pd/0.3APS-CNT < 1Pd/0.6APS-CNT < 1Pd/1.2APS-CNT < 1Pd/2.4APS-CNT < 1Pd/3.6APS-CNT, indicating that functionalization with amino-containing functional groups is able to enhance the surface basicity of CNT support. All these pH variations corroborate the successful surface-functionalization with different amount of APS groups and the effective tuning of the catalysts supports surface basicity.

As suggested previously [27], adsorption bands of amino groups and hydroxyl groups cannot be well resolved using FTIR due to the intersection of bending vibration between N-H and hydroxyl groups within IR range [15]. NIR is superior to FTIR in characterizing amino groups, which can exhibit well-resolved bands in the region between 1000 nm and 2500 nm of wavelength. As shown in Figure 4.10, palladium supported on hydrophilic APS functionalized CNT samples possess two major reflection bands: 1870 nm and 1900 nm indexed to the stretching vibration and deformation vibration for adsorbed H₂O molecules [28], which cannot be observed for relatively more hydrophobic 1Pd/CNT. The reflection peak at 2000 nm is indexed to the combining stretching vibration (ν) and bending vibration (δ) of the amino groups [15, 29], which is hardly visible on 1Pd/CNT without amino-containing surface functional groups. The reflection bands at 2170 and 2265 nm are indexed to the near-infrared optical response of CNT when the electron

transfer from valence band to conduction band ($V_i \rightarrow C_i$) upon the photon absorption at 0.573 and 0.548 eV, respectively [30, 31]. When the APS amount is low, the band strength at 2170 and 2265 nm is lower than 1Pd/CNT because the nonconductive APS surface functional groups covalently σ -bonded onto CNT surface decrease the π -electron density on CNT and subsequently decreases the number of electrons transferring from valence band to conduction band. With the increase of APS amount, the synergistic effect of the electron-donor induction of the low- electronegativity Si and the APS occupation of CNT electron-withdrawing defect sites (e.g., carboxyl groups, lactone, phenol groups [49]) surpasses the π -electron obstruction effect of APS σ -bonding onto CNT surface, increasing the electron density on CNT support which leads to enhanced peak strength at 2170 and 2265 nm. However, the peak strength at 2170 and 2265 nm remains almost unchanged in 1Pd/0.6APS-CNT, 1Pd/1.2APS-CNT, 1Pd/2.4APS-CNT and 1Pd/3.6APS-CNT because the CNT electron-withdrawing defect sites become saturated-occupied by the APS surface-functional groups. Therefore, the UV-vis-NIR spectra further indicate that after surface functionalization, the amino-containing APS functional groups have been immobilized onto the CNT surface and these functional groups have modified the nature of CNT surface chemistry.

Figure 4.10 The NIR spectra of 1Pd/CNT and 1Pd/APS-CNT with different amount of APS.

CO stripping voltammetry is applied to explore the electrochemical activity and the EAS area of these catalysts. As shown in Figure 4.11, CO stripping voltammograms of catalysts surface-functionalized with different amount of APS groups are recorded. Considering the Langmuir–Hinshelwood mechanism for CO electro-oxidation [41], the kinetics, thermodynamics and electrochemical environment of CO molecules as well as the electrochemical state of Pd determine the electro-oxidation potential of CO molecules. It is obvious that CO electro-oxidation peak splits into multiple peaks when CNT support is surface-functionalized with APS. The peak splits are explained by the difference in CO electro-oxidation potential when it is adsorbed on Pd immobilized on different surface sites (e.g., directly on bare CNT, directly on APS and partially on CNT and APS), resulting in different Pd electron densities and surface free energies. Furthermore, the

entrapment and release of CO by the grafted APS groups also contribute to the split of CO electro-oxidation peak considering the perturbation of CO oxidation on Pd surface. As shown in Fig.9, when the APS amount is low, the clustered CO oxidation main peaks tend to present at higher potential. A small amount of APS covalently σ -bonded to CNT surface hinders the electronic interaction between Pd and CNT support, making the CO electro-oxidation reaction more difficult to proceed. Nevertheless, as the APS amount increases, the cluster of CO oxidation main peaks negatively shifts until 1Pd/2.4APS-CNT, implying that CO molecules can be more easily oxidized on Pd particles with smaller particle size and higher electron densities. However, there is a positive shift of the CO oxidation main peaks cluster from 1Pd/2.4APS-CNT to 1Pd/3.6APS-CNT, which may due to the relatively larger Pd nanoparticle of 1Pd/3.6APS-CNT and excess amounts of APS groups. The EAS areas of Pd nanoparticles have been calculated according to the CO stripping voltammetry. As shown in Table 2, the EAS area increases evidently with the increase of APS amount due to the gradual decreased Pd particle sizes which is in agreement with the XRD and TEM observations. Thus the CO stripping voltammetry further substantiates that appropriate amount of amino-containing APS functional groups can facilitate the formation of highly dispersed and small Pd nanoparticles with higher EAS areas. In addition, the negative shift of CO oxidation potentials implies the enhanced catalyst activity for CO electro-oxidation reaction.

Figure 4.11 The CO stripping voltammograms of 1Pd/CNT and 1Pd/APS-CNT with different amount of APS.

Solvent-free benzyl alcohol oxidation over different amount of APS surface-functionalized CNT supported Pd catalysts was investigated and illustrated in Table 4.2. 1Pd/0.3APS-CNT shows the lowest conversion (7.3%) and qTOF ($31,931 \text{ h}^{-1}$) while 1Pd/2.4APS-CNT displays the highest conversion (27.8%) and qTOF ($288,755 \text{ h}^{-1}$). Low contents of APS covalently σ -bonded onto CNT surface hampers the electron conduction between Pd and CNT support, making the reaction more difficult to proceed which is in agreement with the CO stripping voltammetry result. Increasing the APS amount evidently increases the catalytic activity until 1Pd/2.4APS-CNT, the most highly active catalyst in CO electro-oxidation. The sharply decreased conversion and qTOF of 1Pd/3.6APS-CNT are resulted from the decreased Pd particle exposure due to the excess amounts of grafted APS groups which possibly form alkanolamine through oligomerization and polymerization on the CNT support. As shown in Table 2, the catalytic performances of these catalysts for aerobic benzyl alcohol oxidation are in accordance with the CO electro-oxidation results. The presence of toluene as the by-product indicates that the Pd nanoparticles are in their reduced state (Pd^0) [44]. Although 1Pd/2.4APS-CNT possesses the highest conversion and qTOF, the selectivity toward benzaldehyde is relatively unsatisfactory owing to the high selectivity toward benzoic acid.

Table 4.2 pH and Catalytic results of benzyl alcohol oxidation over 1Pd/CNT, 1Pd/0.3APS-CNT, 1Pd/0.6APS-CNT, 1Pd/1.2APS-CNT, 1Pd/2.4APS-CNT and 1Pd/3.6APS-CNT catalysts

Catalyst	pH	Pd ^b (wt.%)	EAS ^c (m ² g ⁻¹)	Conversion (%)	Selectivity (%)			qTOF ^d (h ⁻¹)
					Benzaldehyde	Toluene	Benzoic acid	
1Pd/CNT	6.2	0.96	12.1	17.1	95.3	2.1	2.6	177,483
1Pd/0.3APS-CNT	7.7	0.94	13.6	7.3	93.9	3.7	2.4	31,931
1Pd/0.6APS-CNT	8.3	0.95	13.8	15.0	96.6	0.4	3.1	135,380
1Pd/1.2APS-CNT	9.0	0.97	14.2	21.4	90.5	5.8	3.7	211,320
1Pd/2.4APS-CNT	9.1	0.98	14.3	27.8	91.9	1.2	6.9	288,755
1Pd/3.6APS-CNT	9.2	1.01	14.5	7.9	96.5	2.5	0.9	35,496

^a Reaction conditions: catalyst, 10mg (the amount of Pd is 1 wt.% of catalyst, 0.1mg);

benzyl alcohol, 50mmol; O₂, 20mL min⁻¹; temperature, 160°C; time, 1h.

^b Metal content was obtained by ICP.

^c EAS areas were measured from CO stripping data.

^d qTOF is defined as the number of benzyl alcohol molecules converted in 1h on one active site; the number of active sites (Pd atoms exposed on the surface) is determined by EAS value [43] considering Pd content obtained from ICP, and subtracted the CNT effect (conversion ~5%).

4.4 Effects of reaction time, temperature and oxygen flow rate

1Pd/2.4APS-CNT, verified to possess the optimal catalytic performance in the solvent-free benzyl alcohol oxidation, has been investigated in detail. As depicted in Figure 4.12, the time course of 1Pd/2.4APS-CNT for oxidation of benzyl alcohol has been monitored constantly. The benzyl alcohol conversion increases monotonically along with the declined selectivity toward benzaldehyde with the reaction time duration. The qTOF is rather low ($151,419 \text{ h}^{-1}$) at the first 0.5 h of reaction; it then rises to $266,845 \text{ h}^{-1}$ at 1 h and progressively decreases subsequently. The poor qTOF at the first 0.5 h is possibly due to the reduction of Pd precursors by alcohols and the gradual decrease of the qTOF after 1 h is ascribed to the diminished amount of reactant benzyl alcohol. The decrease of selectivity toward benzaldehyde is contributed by the further oxidation to form benzoic acid.

Figure 4.12 Time course of 1Pd/2.4APS-CNT for oxidation of benzyl alcohol (reaction condition: benzyl alcohol/Pd = 1000 mol/g; O₂ flow rate = 20 mL min⁻¹; temperature = 160 °C; stirring rate = 1200 rpm).

The effects of temperature and molecular oxygen flow rate have been investigated and the results are summarized in Table 4.3. The catalytic activity is not noticeable at low temperature. Furthermore, toluene is formed in a large quantity at low temperature due to benzyl alcohol hydrogenolysis [44]. As the temperature increases, the conversion of benzyl alcohol increases with the decline of selectivity towards toluene, while high temperature favors the deep oxidation of benzaldehyde to form benzoic acid. The activation energy over 1Pd/2.4APS-CNT catalyst is 44.65 kJ/mol, which is similar to that of noble metal catalysts supported on TiO₂ as reported by Enache et al. (45.8 kJ/mol) [50] and remarkably higher than the Pd catalyst supported on mesoporous silica SBA-16 material where the reaction is limited by mass diffusion (12.3 kJ/mol) [51], [52]. The O₂ flow also shows significant effect on the catalytic performance. Benzyl alcohol can be converted to benzaldehyde by dehydrogenation in the absence of oxygen (conversion 4.7%), along with hydrogen as the co-product. The selectivity toward benzaldehyde is rather low (71.8%) because benzyl alcohol, as the acceptor of hydrogen undergoes the hydrogenolysis due to the lack of O₂. The conversion increases as the oxygen flow rate is elevated until the flow rate reaches 20 mL min⁻¹, followed by an abrupt drop at 30 mL min⁻¹ because excess oxygen favors the oxidation of Pd catalyst. With the increase of O₂ flow rate, the selectivity toward toluene is low because oxygen is a good hydrogen acceptor, reducing the coverage of hydrogen on Pd surface and subsequently decreasing the extent of hydrogenolysis which yields toluene.

Table 4.3 Effect of reaction conditions for 1Pd/2.4APS-CNT on benzyl alcohol oxidation^a

Entry	Temperature (°C)	O ₂ flow rate (mL min ⁻¹)	Conversion (%)	Selectivity (%)		
				Benzaldehyde	Toluene	Benzoic acid
1	120	20	7.8	90.9	9.1	0
2	140	20	14.8	94.0	5.4	0.6
3	160	0	4.7	71.8	28.2	0
4	160	5	9.5	87.9	12.1	0
5	160	10	13.1	88.4	10.8	0.8
6	160	20	26.5	96.6	1.3	2.0
7	160	30	12.8	96.7	1.0	2.3

^a Reaction conditions: benzyl alcohol/Pd = 1000 mol/g; reaction time = 1 h; stirring rate = 1200 rpm.

^b qTOF is defined as the number of benzyl alcohol molecules converted in 1h on one active site; the number of active sites (Pd atoms exposed on the surface) is determined by EAS value [43] considering Pd content obtained from ICP, and subtracted the CNT effect (conversion ~5%). Table 4.3 avoiding using qTOF since the qTOF might be negative when oxygen flow rate is zero.

The recyclability is considered as a crucial factor in evaluating a heterogeneous catalyst in a multiphase system. The active components with poor stability and recyclability leaches out during the reaction course, leading to the formation of active homogeneous catalyst at the cost of losing catalytic activity during consecutive runs. The recyclability of 1Pd/2.4APS-CNT in solvent-free selective oxidation of benzyl alcohol using molecular oxygen has been investigated. The catalyst was recovered by washing with acetone and drying at 60 °C, and subsequently reused in the next run of reaction. Figure 4.13 displays the recyclability of 1Pd/2.4APS-CNT for 5 consecutive reaction cycles. The loss of catalytic activity and selectivity is moderate for these five cycles, indicating that the loss of catalyst during recovery is insignificant. The Pd content after five consecutive cycles is almost the same as the as-produced catalyst with no leaching of Pd due to the strong metal-support interaction after modifying the CNT surfaces by APS. Therefore, APS-functionalized CNT supported Pd catalyst not merely improve the catalytic performance but also enhance the resistance against deactivation.

Figure 4.13 Recyclability of 1Pd/2.4APS-CNT catalyst for selective solvent-free oxidation of benzyl alcohol (reaction conditions: benzyl alcohol/Pd = 1000 mol/g; O₂

flow rate = 20 mL min⁻¹; temperature = 160 °C; reaction time = 1 h; stirring rate = 1200 rpm).

4.5 Discussion

Upon hydrophilic amino-containing APS surface functionalization, palladium precursors are easily adsorbed, and Pd nanoparticles are uniformly immobilized on the surface-modified CNT support with a narrow size distribution and improved metal-support interaction along with the finely tuned basicity surrounding Pd nanoparticles. All these parameters are essential to account for the significantly improved catalytic performances, in which the surface basicity and Pd nanoparticle size are two crucial factors controlling the catalytic activity based on electro-active surface area (qTOF) and selectivity, yet the surface basicity also has impact on the Pd particle size and size distribution, leading to the complex and ambiguous explanation on the impact of individual factors and their interaction upon the catalytic behavior. To unravel the effects of each factor and their interaction with clarity, multivariate analysis modeling was applied to establish a second order polynomial regression with MATLAB to fit the two variables (x_1 : Pd size, x_2 : pH value) and two dependent variables (y_1 : qTOF, y_2 : selectivity toward benzaldehyde). The contour plots of qTOF and selectivity are shown in Figure 4.14, showing a rational investigation of the effect of each experimental variable on the dependent variables. High qTOF can be obtained at small Pd size, along with mildly basic surfaces. Similarly, high selectivity can be achieved at small Pd size and mild basicity. Therefore, the controlling of Pd size and surface basicity influences the catalytic behavior.

Figure 4.14 Contour plots of (a) qTOF; (b) selectivity toward benzaldehyde with Pd size and pH as the variables.

4.6 Summary

In this chapter, various organosilanes (APS, ATMS and HMDS) surface-functionalized CNT supported Pd catalysts were prepared following a modification scheme along with a metal adsorption-reduction step. Catalytic performance of these as-

synthesized catalysts has been examined in the solvent-free selective oxidation of benzyl alcohol with molecular oxygen. The reaction results suggested that both the variety and amount of surface-functional groups on CNT support evidently influenced the catalytic performance. An appropriate amount of APS surface-modified CNT supported Pd catalyst turned out to be the optimal catalyst as a result of the finely-tuned surface basicity, small Pd particle size with narrow size distribution, high electron density and enhanced metal-support interaction. Among all these catalysts, 1Pd/2.4APS-CNT was explored with a remarkably high q_{TOF} of $288,755\text{ h}^{-1}$ for benzyl alcohol oxidation. This work has been published in *Applied Catalysis B: Environmental* (Yan et al. *Applied Catalysis B: Environmental*, 2014, 156, 385–397); reuse in this chapter is under the permission of Elsevier Global Rights Department.

List of abbreviations

APS	3-aminopropyltriethoxysilane
ATMS	[3-(2-aminoethylamino) propyl] trimethoxysilane
CNTs	Multi-Walled Carbon Nanotubes
CV	Cyclic Voltammogram
EA	Ethyl Acetate
EAS	Electrochemical Active Surface
GC	Chromatography
HMDS	Hexamethyldisilazane
ICP	Inductively coupled plasma
NIR	Near-infrared spectroscopy
TEM	Transmission Electron Microscopy
TOF	Turnover Frequency
XPS	X-ray Photoelectron Spectroscopy
XRD	X-Rays Diffraction

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Chapter 5 Palladium nanoparticles supported on CNT functionalized by rare earth oxides for solvent-free aerobic oxidation of benzyl alcohol

Rare earth elements have demonstrated a broad range of applications in catalysis. Rare earth oxides-based heterogeneous catalysts have been applied in various organic chemistry reactions such as the redox, aldolization, alcohol dehydration, ketone formation, aromatic compounds alkylation, ring-open, coupling reactions and so forth due to the redox and acid-base properties of ceria [1, 2]. Numerous cationic rare earth metal complexes have been synthesized to perform as the catalysts for olefin polymerization reactions [3, 4]. Furthermore, rare earth oxides also attract various curiosities as a structural and electronic promoter to improve the catalyst performance of numerous catalysts over conventional supports such as silica, alumina, titania and so forth [5-10]. Well known for the lattice oxygen storage capability, rare earth oxides have been applied into automotive catalysts [11, 12], improved catalyst for soot oxidation [13], and industrial catalysts for removal of organics from wastewaters [14, 15]. Owing to the improved basic strength and their contribution to the reducibility increase, rare earth oxides have highly promoted the performance after their modifying Pt/SiO₂ catalysts for CO oxidation [16].

In terms of catalyst supports, such as metal oxides [17] and carbonaceous materials [18, 19], they play a pivotal role in the catalytic system. Carbon nanotubes (CNTs) are among the headlines of nanotechnology, particularly catalysis, in virtue of the high purity eradicating self-poisoning, thermal stability, electrical conductivity, impressive mechanical properties, high accessibility of the active phase and absence of microporosity thus reducing the mass diffusion and intra-particle transfer effects in reaction

medium [20-22]. As for catalysis, the metal oxides functionalities contribute to the control of the properties such as the electron conductivity, polarity, hydrophilicity and surface chemistry including amphoteric property in order to develop the CNT-based catalysts with enhanced catalytic performance for certain reactions. Zhou et al. reported that the manganese dioxide functionalized CNTs supported platinum catalysts possess higher electrochemical active surface area and better methanol electro-oxidation activity than Pt/CNTs [23].

CNT as catalyst support has been extensively explored [24, 25]. Nevertheless, reports related to rare earth oxides applied as surface functionalities of CNTs supported catalysts are limited. Hence, this study is aimed to prepare rare earth oxides LnO_x ($\text{Ln}=\text{La}, \text{Ce}, \text{Sm}, \text{Gd}, \text{Er}, \text{Yb}$) functionalized CNTs supported palladium catalysts considering the possible surface chemistry and electron property modification that the rare earth oxides would bring to the catalyst system. The obtained catalysts are evaluated through the aerobic oxidation of benzyl alcohol with molecular oxygen, which is a vitally important intermediate reaction to transform functional groups in organic synthesis and meanwhile a model aromatic alcohol oxidation reaction employed by laboratory study. The investigation and discussion of the correlation of the catalysts structure, surface chemistry, electrochemical activity and catalytic performance will be rendered in detail.

5.1 Characterization of the properties of rare earth oxides functionalized CNT supported Pd catalysts

Figure 5.1 XRD diffraction patterns of Pd/5Ln-CNT.

X-ray diffraction and TEM are applied as techniques to characterize the crystalline structural conformation and morphology of materials. Figure 5.1 displays the XRD patterns of Pd/LnO_x-CNT samples with different rare earth oxides. The diffraction peaks at 26.01 ° and 42.80 ° are respectively ascribed to the (0 0 2) and (1 0 0) facets of graphitic CNT [30]. The diffraction peaks at 40.00 °, 46.07 °, 68.30 ° shown in each catalyst are in correspondence with the (1 1 1), (2 0 0), and (2 2 0) facets respectively of palladium face-centered cubic (FCC) structure. According to Bragg's Law [31], the lattice d-spacing of (1 1 1) plane calculated is approximately 0.225 nm which is further verified by HRTEM shown in Figure 5.2. Accordingly, rare earth

oxides surface functionalities didn't result in lattice contraction within Pd crystal facets. The approximate full width at half max (FWHM) of 1.09° at the peak of 40.00° is in agreement with the Pd particles average size of 8 nm for 1Pd/CNT catalyst according to the Scherrer Equation [32, 33]. Similarly, the FWHMs of 1.14° at 40.00° is indexed to the average Pd size around 7 nm in 1Pd/5Er-CNT and 1Pd/5Yb-CNT catalysts. The FWHMs of 1.24° at 40.00° correspond to the Pd particle average size around 6 nm for 1Pd/5Gd-CNT, and 1Pd/5La-CNT catalysts. The FWHMs of 1.43° at 40.00° indicate the Pd grain average size of about 4 nm in Pd/5Sm-CNT and 1Pd/5Ce-CNT catalysts. Since the hydrophilic rare earth oxides functionalities can improve the hydrophilicity of CNT surface then increase the affinity to the aqueous palladium chloride, the deposition of Pd precursor becomes easier, and favors the formation of smaller Pd particles. Moreover, the positively charged rare earth cation possesses great affinity to the $\text{PdCl}_2(\text{OH})_2^{2-}$ precursor, also contributing to the small and highly dispersed Pd nanoparticles. This result is further corroborated by the TEM observations and Pd particle size distribution histogram shown in Figure 5.2. No distinct XRD diffraction peak for rare earth oxides can be detected, implying the rare earth oxides have been homogeneously dispersed over the CNT surfaces. Since the amount of rare earth oxides were not high enough, grains of rare earth oxides as well as their contact with Pd particles were hardly perceived on HRTEM images. The rare earth cationic precursors were chemically anchored to oxygen-containing groups on CNT surfaces. Thus the rare earth oxides were evenly deposited and the grain size was well-controlled on the level of nano-dimensions.

Figure 5.2 TEM images and Pd particle size distribution histograms: (a) Pd/5La-CNT; (b) Pd/5Ce-CNT; (c) Pd/5Sm-CNT; (d) Pd/5Gd-CNT; (e) Pd/5Er-CNT; (f) Pd/5Yb-CNT.

Figure 5.3 FTIR spectra of pyridine adsorption on 1Pd/CNT, 1Pd/5La-CNT, 1Pd/5Ce-CNT, 1Pd/5Sm-CNT, 1Pd/5Gd-CNT, 1Pd/5Er-CNT and 1Pd/5Yb-CNT catalysts at different temperatures.

In situ Fourier Infrared spectroscopy with pyridine adsorbed on surface of catalysts has been widely applied to investigations of surface Lewis and Brønsted acidic sites [34-37]. As shown in Figure 5.3, FTIR spectra were recorded of pyridine adsorption on Pd/CNT as well as different rare earth oxides functionalized CNT supported palladium catalysts with the same rare earth element content (5 wt.%) along with the same palladium content (1 wt.%) and subsequently desorption at different temperatures. The pyridine molecule is retained on the surface in three modes: (1) interaction between the N electron pair and the hydrogen atom of OH group, (2) proton transfer from surface to pyridine (Brønsted acidity) and (3) pyridine molecule coordination to electron deficient sites (Lewis acidity) [38]. Ring vibrations in the range from 1400 to 1700 cm^{-1} were used to distinguish between pyridine adsorbed on Lewis and Brønsted acidic sites. FTIR bands centered at 1609 cm^{-1} , 1586 (or 1570, 1582, 1585, 1587) cm^{-1} , 1500 (or 1496, 1487) cm^{-1} and 1453 (or 1447, 1452, 1454, 1457) cm^{-1} have been indexed to the 8a and b, 19a and b pyridine vibrational modes attributed to electron transfer at Lewis acidic surface sites respectively. Whereas the bands at 1642 (or 1635, 1640, 1644) cm^{-1} and 1544 (or 1537, 1545, 1546, 1547) cm^{-1} are assigned to v8a and v8b vibrational modes of pyridine due to proton transfer (i.e., hydrogen bond) at Brønsted acidic sites [37]. It is obvious that Lewis acid site density and strength are both higher than those of Brønsted acidic site in 1Pd/CNT and 1Pd/5Ln-CNT catalysts which indicates that electron deficient sites are dominant. At 50 °C, the much more intense bands at 1586 cm^{-1} , 1500 cm^{-1} and 1543 cm^{-1} on

1Pd/CNT indicates that it possesses higher density of Lewis acid sites than those functionalized by rare earth oxides nanoparticles under relatively mild conditions. This indicates that at a relatively low temperature (e.g., 50°C), the amount of the surface oxygen-containing species (e.g., carbonyl and carboxyl) on CNT decreases after the surface-functionalization with rare earth oxides which may overlap the oxygen-containing species. However, an abrupt decline of Lewis acid site density occurs on 1Pd/CNT as the temperature increases, which, on the contrary not has been observed in spectra of 1Pd/5Ln-CNT catalysts, implying that the oxygen-containing species on CNT surface decreases with the increase of temperature, in agreement with the results by Guo et al [39]. Additionally, this implies the rare earth oxides functionalized CNT supported Pd catalysts possess higher thermal stability of surface Lewis acid sites than 1Pd/CNT catalyst as well. Moreover, the shifts or splits of each band demonstrated the different types of Lewis/ Brønsted acidic sites that the rare earth oxides introduced onto the CNT surface after functionalization. Among all the catalysts, the most complexity of the multiple IR bands indicates the largest number of acid site types present on Pd/5Sm-CNT with eminent thermal stability. These acidic sites can play a vital role in alcohol dehydrogenation reaction [40-44], which is commonly present in the mechanism of benzyl alcohol oxidation reaction with molecular oxygen [45].

Figure 5.4 (a) Cyclic voltammetry curves (CVs) of 1Pd/CNT and 1Pd/5Ln-CNT catalysts in 1M KOH aqueous solution with a scan rate of 50 mVs^{-1} ; (b) magnification of the selected area in (a) presenting Pd-O reduction peaks.

Surface acidic sites on catalysts were characterized through pyridine adsorbed FRIR spectra, while the surface basicity was associated with their electro-chemical properties, especially the electron donor property [38]. Cyclic voltammetry measurements were carried out on 1Pd/CNT and 1Pd/5Ln-CNT catalysts, as shown in Figure 5.4. Since the larger area enclosed by CV background implies a higher electron density [39], the rare earth oxides functionalities can regularly improve the electron densities of each catalyst. In Figure 5.4, the background of CV signals are observed with an evident decrease in the area enclosed in the sequence of: 1Pd/5La-CNT > 1Pd/5Ce-CNT > 1Pd/5Sm-CNT $\approx$ 1Pd/5Gd-CNT > 1Pd/5Er-CNT > 1Pd/5Yb-CNT > 1Pd/CNT. Rare earth oxides are well known for their surface electron donor

properties [46-49], which favours the enlargement of areas enclosed by CV curves, since the more redox active sites or electron donors on CNT, the larger capacitance and CV background are [50]. The sequence mentioned above is in tune with lanthanide contraction: basicity of rare earth oxides, which is related to electron donor properties, declines with the contraction of rare earth cation radius [51]. The absence of palladium oxide (Pd-O) reduction peak at 0.1V in rare earth oxides modified CNT supported Pd catalysts, except 1Pd/5Gd-CNT, indicates that Pd nanoparticles are more easily reduced to zero-valent state (Pd^0) over rare earth oxides surface functionalized CNT supports. Surface basicity contributes to the formation of small Pd nanoparticle size and narrow size distribution along with an enhanced metal-support interaction, which has been reported by Chen et al. and they suggested that the basicity can significantly impact the catalytic performance in the aerobic oxidation of benzyl alcohol [28]. Furthermore, the electron density is another crucial factor for catalytic performance.

CO stripping voltammetry was performed to characterize each catalyst through electro-oxidation reaction of carbon monoxide. In CO stripping, CO monolayer primarily adsorbed on catalysts will be electro-oxidized to CO_2 at initially a negative voltage and along with the increased sweeping voltage of the working electrode immersed in 1M of KOH aqueous electrolyte solution. Based on cyclic voltammetry, CO stripping is a practical method to measure the electrochemical active surface (EAS) area of Pd nanoparticles at low Pd loadings [52], because of the low electrical signals ascribed to the release of hydrogen atoms bonded to Pd surfaces as well as the uncertainty caused by the background subtraction [39]. The Langmuir–Hinshelwood

mechanism is normally accepted as the model for CO electro-oxidation, where adsorbed OH formed on the Pd surface by dissociative adsorption of H₂O reacts with the adsorbed CO [53].

The KOH aqueous electrolyte neutralizes the H⁺ and pushes the reaction moving forward. Thus CO electro-oxidation potential relies upon the kinetics, thermodynamics and electrochemical state of Pd nanoparticles. Figure 5.5 presents the CO stripping voltammograms of 1Pd/CNT and 1Pd/5Ln-CNT catalysts. The negative shifts of onset potentials for CO electro-oxidation indicate the higher catalytic activity for the onset of CO electro-oxidation reaction, suggesting that it is easier to initiate the CO oxidation using rare earth oxides functionalized 1Pd/5Ln-CNT catalysts. Accordingly, the rare earth oxides functionalized CNT supported Pd catalysts possess the higher onset catalytic activity than non-functionalized Pd/CNT catalyst, which may due to the improved electron density, electron transition capability and the enhanced metal-support interactions. Among all these catalysts, the 1Pd/5Sm-CNT possesses the highest onset catalytic activity for CO oxidation. The EAS areas of Pd particles were calculated according to CO stripping voltammetry, with the assumption that the oxidation of CO monolayer adsorbed on surface of 1 cm² of Pd nanoparticles requires 420 μC of electric charge [54, 55]. The results show that the electrochemical active surface areas are in correspondence with the XRD and TEM measurements (shown in Table 1). Modification with rare earth oxides, especially Sm₂O₃ and CeO₂, facilitates EAS increase in catalysts

due to the smaller particle sizes and the higher dispersion of Pd nanoparticles.

Figure 5.5 CO stripping voltammograms of 1Pd/5La-CNT, 1Pd/5Ce-CNT, 1Pd/5Sm-CNT, 1Pd/5Gd-CNT, 1Pd/5Er-CNT, 1Pd/5Yb-CNT and 1Pd/CNT catalysts

5.2 Effects of different rare earth oxides surface functionalities

We applied the solvent-free oxidation of benzyl alcohol with molecular oxygen as a model reaction to examine these Pd/CNT and Pd/5Ln-CNT catalysts, in order to elucidate the effect of surface rare earth oxides functionalities on catalytic performance. The results are listed in Table 5.1, where qTOF was determined as the number of converted benzyl alcohol molecules per hour over the number of active sites where the number of active sites (i.e., Pd atoms exposed on the particle surface) was determined by EAS value with the Pd content obtained from ICP measurements, subtracting the non-catalytic effect (i.e., ~5% of benzyl alcohol conversion at 160 °C). According to ICP test results in Table 1, the increased Pd contents upon functionalization with rare earth oxides suggest the enhanced surface hydrophilicity which can reduce the adsorption barrier of palladium aqueous precursor onto the support surface. Dehydrogenation of benzyl alcohol already occurs to form benzaldehyde and coproduct molecular hydrogen in the absence of O₂. Oxygen is a great hydrogen acceptor to consume H₂ [45]. The main product benzaldehyde is a non-enolizable aldehyde, which limits the number of byproducts. Primary byproducts include toluene from hydrogenolysis of C-O bond of benzyl alcohol where hydrogen molecule is formed from dehydrogenation reaction on Pd in reduced state (Pd⁰) and benzoic acid formed by hydration of benzaldehyde followed by the dehydrogenation reaction [45].

In addition, the surface basicity of catalysts favours the disproportionation of benzaldehyde (Cannizzaro reaction), producing benzoic acid and benzyl alcohol [56].

As shown in Table 5.1, the catalytic activity is remarkably improved upon the functionalization with rare earth oxides owing to the smaller Pd particle size, improved surface chemistry, enhanced metal-support interaction and electrochemical property of the active phase. Among all the catalysts, 1Pd/5Sm-CNT presents the best catalytic performance with a conversion of 29.6% and an outstanding qTOF of 253,842 h⁻¹, which is 1.5 times that of 1Pd/CNT, owing to the smallest size of Pd nanoparticles [57], improved metal-support interaction, appropriate surface basicity and the abundant thermal stable surface acid sites over 1Pd/5Sm-CNT surface. The surface basic site has been reported to cleave the O-H bond to produce alkoxide intermediate while the surface acid site participates in producing and transferring H₂ in dehydrogenation of benzyl alcohol [44], a significant step in its oxidation reaction, since surface acid sites possess better affinity to H₂ [58-60]. Nevertheless, the high activities are accompanied by a large amount of toluene as byproduct, so as to decrease the benzaldehyde selectivity. The formation of toluene further verified the Pd is in reduced state (Pd⁰) [45], which favours its producing and coverage of H₂, facilitating the hydrogenolysis of benzyl alcohol to form toluene when O₂ is not sufficiently supplied or the reaction rate of O₂ consuming H₂ is not rapid enough. The relatively lower selectivity toward toluene of 1Pd/5Sm-CNT than other rare earth oxides functionalized catalysts is caused by the abundant amount of types of acid sites absorbing the hydrogen from Pd surface on 1Pd/5Sm-CNT, reducing the amount of H₂ on Pd surface. Considering the highest conversion and appropriate

selectivity toward benzaldehyde, the Sm_2O_3 was selected as the optimal surface functionality in the following study.

Table 5.1 Catalytic results of benzyl alcohol oxidation over 1Pd/CNT and 1Pd/5Ln-CNT catalysts. ^a

Catalyst	Pd content (wt.%) ^b	Ln content (wt.%) ^b	EAS ^c (m ² g ⁻¹)	Conversion (%)	Selectivity (%)			qTOF ^d (h ⁻¹)
					Benzal dehyde	Toluene	Benzoic Acid	
1Pd/CNT	0.78		12.8	17.2	91.3	7.1	1.6	169,163
1Pd/5La-CNT	0.81	2.81	18.9	26.7	88.6	11.4	0	203,777
1Pd/5Ce-CNT	1.25	1.64	18.4	25.8	85.2	14.4	0.4	201,597
1Pd/5Sm-CNT	0.79	2.06	17.2	29.6	90.4	7.2	2.4	253,842
1Pd/5Gd-CNT	1.08	2.59	14.7	24.5	81.4	18.6	0	235,437
1Pd/5Er-CNT	0.93	2.78	13.9	23.4	84.2	15.8	0	234,942
1Pd/5Yb-CNT	0.91	2.86	13.0	23.0	85.6	13.9	0.5	245,746

^a Reaction conditions: catalyst, 10mg (the amount of Pd is 1 wt.% of catalyst, 0.1mg);

benzyl alcohol, 50mmol; O₂, 20mL min⁻¹; temperature, 160°C; time, 1hr.

^b real metal content was tested by ICP.

^c EAS areas were deduced from data of CO stripping.

^d qTOF is defined as the number of converted benzyl alcohol molecules in 1hr over one active site; the number of active sites (Pd atoms exposed on the surface of particle) is determined by EAS value [55] considering Pd content obtained from ICP, and subtracted the non-catalytic effect (conversion ~5%).

5.3 Effects of the samarium oxides content

CNT functionalized with 2.5 wt.%, 5 wt.%, 7.5 wt.%, 10 wt.% content of Sm in the form of Sm_2O_3 and loaded with 1 wt.% of Pd were prepared for comparison. XRD patterns of samarium oxide functionalized CNT supported Pd catalysts are presented in Figure 5.6. The peak width at half height of the peak at 40.00° , related to the characteristic (1 1 1) plane of Pd, increases with the growth of Sm_2O_3 content, implying the decrease of Pd nanoparticle size according to Scherrer equation, which has been further substantiated by TEM observations shown in Figure 5.7. The Pd nanoparticle size decreases in the series of 4.3 nm, 3.7 nm, 3.3 nm and 3 nm, as the Sm_2O_3 content increases in the order of 2.5 wt.%, 5 wt.%, 7.5 wt.% and 10 wt.%. The more amount of Sm_2O_3 functionality facilitates the higher hydrophilicity of CNT surface which favours smaller Pd nanoparticles. Meanwhile, peaks centered at 27.76° and 31.94° , assigned to (1 1 1) and (2 0 0) planes of Sm_2O_3 , emerge and intensify as the Sm content increases from 2.5 wt.% to 10 wt.% in the form of Sm_2O_3 , which enables the formation of larger amount of crystal structure of Sm_2O_3 .

Figure 5.6 XRD patterns for 1Pd/Sm₂O₃-CNT with Sm content of 2.5wt.%, 5wt.%, 7.5wt.% and 10wt.%.

Figure 5.7 TEM images and Pd particle size distribution histograms of various amount of Sm₂O₃ functionalized CNT supported Pd catalysts.

CV measurements were performed and cyclic voltammograms were shown in Figure 5.8. The areas enclosed by CV curves are observed with an evident decrease in the sequence of: 1Pd/2.5Sm-CNT > 1Pd/5Sm-CNT > 1Pd/7.5Sm-CNT > 1Pd/10Sm-CNT. Small content of rare earth functionalized CNT supported Pd catalyst has larger

capacitance and CV background due to the remarkable electron donating properties of Sm_2O_3 . Nevertheless, the capacitance and CV background will decline with the further increase of rare earth oxides content due to the abrupt decrease of the electron conductor (i.e., CNT) content. The redox signal peak of Pd-O bond at ca. -0.09 V is only discernible for 1Pd/2.5Sm-CNT, indicating that the higher content of Sm_2O_3 favours fully reduced Pd (Pd0) generation and stabilizes the zero-valent status of Pd (Pd0) nanoparticles.

Figure 5.8 Cyclic voltammograms (CVs) of 1Pd/2.5Sm-CNT, 1Pd/5Sm-CNT, 1Pd/7.5Sm-CNT and 1Pd/10Sm-CNT catalysts in 1M KOH electrolyte solution with a scan rate of $50\text{mV}\cdot\text{s}^{-1}$.

Figure 5.9 CO stripping voltammograms of 1Pd/2.5Sm-CNT, 1Pd/5Sm-CNT, 1Pd/7.5Sm-CNT and 1Pd/10Sm-CNT catalysts

CO stripping voltammetry was carried out to measure the EAS areas of 1Pd/Sm₂O₃-CNT, as shown in Figure 5.9. The EAS area initially increases when Sm content rises from 2.5 wt.% to 5 wt.% and subsequently declines as Sm content rises up to 10 wt.%.

The Sm_2O_3 functionalities facilitate the surface hydrophilicity of CNT and hence favour the formation of smaller Pd nanoparticles which possess higher EAS area without the presence of agglomeration at low Sm_2O_3 loadings. Nonetheless, when Sm_2O_3 content gets high enough to form more Sm_2O_3 crystalized grains, the metal-support interaction is enhanced with smaller Pd nanoparticles which may reduce the surface exposure of Pd nanoparticles. The mass transfer resistances resulted from the uneven surface after functionalization by large amount of Sm_2O_3 also hampers the contact between Pd and CO molecules and thus result in a smaller EAS area. In addition, higher Sm_2O_3 loadings lead to much more direct contact between small Pd nanoparticles and Sm_2O_3 which may reduce the exposure of Pd effective surface to the liquid phase. Among all these samarium oxide functionalized CNT-supported Pd catalysts, 1Pd/5Sm-CNT retains the largest EAS area. Meanwhile, the 1Pd/5Sm-CNT catalyst possesses the lowest onset potential for CO electro-oxidation reaction, indicating its highest onset electrochemical activity for CO electro-oxidation as the model reaction.

To quantitatively evaluate the effect of Sm_2O_3 surface functionalities on the catalytic performance, benzyl alcohol oxidation over 1Pd/ Sm_2O_3 -CNT with different content of Sm_2O_3 was investigated and illustrated in Table 5.2. Pd loading of each catalyst was determined through ICP measurement. The catalytic activity is improved when Sm_2O_3 is doped on CNT surface due to the decreased Pd particle size and synergistic effect from metal-support and metal-functionalities interactions. 1Pd/5Sm-CNT catalyst possesses the highest benzyl alcohol conversion value of 29.6%. Further increasing the Sm_2O_3 loading elevates the qTOF value and selectivity toward benzaldehyde at the sacrifice of EAS area along with the lower conversion value of the substrate benzyl alcohol. The

explanation for decrease in EAS area has been illustrated that large amount of Sm_2O_3 functionality enhances the metal-support interaction and the contact area between Pd, Sm_2O_3 and CNT. Both of them decline the exposure of Pd effective area, leading to lower conversion of benzyl alcohol. The trend of qTOF value implies the activity of supported Pd catalysts is primarily dependent on the electrochemical active surface, electron density and surface chemistry surrounding the active phase. Small amount of Sm_2O_3 facilitate the formation of toluene and hence the selectivity toward benzaldehyde is low (83.3%). As the Sm_2O_3 content increases, the selectivity toward benzaldehyde is improved, indicating that the functionalization with an appropriate amount of Sm_2O_3 reduces the formation of byproducts. On account of the highest yield toward the main product benzaldehyde, 1Pd/5Sm-CNT is considered as the optimal catalyst in this study.

Table 5.2 Catalytic results of benzyl alcohol oxidation over 1Pd/2.5Sm-CNT, 1Pd/5Sm-CNT, 1Pd/7.5Sm-CNT and 1Pd/10Sm-CNT catalysts. ^a

Catalyst	Pd content (wt.%) ^b	Ln content (wt.%) ^b	EAS ^c (m ² g ⁻¹)	Conversion (%)	Selectivity (%)			qTOF ^d (h ⁻¹)
					Benzalde hyde	Toluene	Benzoic Acid	
1Pd/CNT	0.78		12.8	17.2	91.3	7.1	1.6	169,163
1Pd/2.5Sm-CNT	0.72	0.66	15.9	28.1	83.3	15.8	0.9	257,853
1Pd/5Sm-CNT	0.79	2.06	17.2	29.6	90.4	7.2	2.4	253,842
1Pd/7.5Sm-CNT	0.83	4.20	11.7	26.1	93.6	4.4	2.0	318,552
1Pd/10Sm-CNT	0.95	6.52	10.3	23.5	95.7	1.5	2.8	318,760

^a Reaction conditions: catalyst, 10mg (the amount of Pd is 1 wt.% of catalyst, 0.1mg); benzyl alcohol, 50mmol; O₂, 20mL min⁻¹; temperature, 160°C; time, 1hr.

^b real metal content was tested by ICP.

^c EAS areas were deduced from data of CO stripping.

^d qTOF is defined as the number of converted benzyl alcohol molecules in 1hr over one active site; the number of active sites (Pd atoms exposed on the surface of particle) is determined by EAS value [55] considering Pd content obtained from ICP, and subtracted the non-catalytic effect (conversion ~5%).

5.4 Reaction time course and other investigations of catalytic performance

The XPS spectra of Pd 3d and O 1s have been investigated as shown in Figure 5.10. The Pd 3d peaks were convoluted to Pd⁰ and Pd²⁺ two states. The ratios of Pd⁰/(Pd⁰+Pd²⁺) in Pd/CNT and Pd/5Sm-CNT are 42.3% and 69.7% respectively, indicating the electron donor property of Sm₂O₃ in consistent with the CV results which subsequently enhances the Pd electron density. The shift of 3d_{3/2} and 3d_{5/2} binding energy peaks of Pd²⁺ towards reduced forms after surface-functionalization with Sm₂O₃ illustrates the lower oxidation extent of Pd or the formation of Pd-Sm₂O₃ complex [61]. The fractions of C-O/C=O of Pd/CNT and Pd/5Sm-CNT are quite close. Nonetheless the apparent increase in lattice oxygen of Pd/5Sm-CNT compared to Pd/CNT is explained by the presence of lattice oxygen in Sm₂O₃ surface functionality.

Figure 5.10 XPS spectra: (a) Pd 3*d* spectra; (b) O 1*s* spectra of Pd/CNT and Pd/5Sm-CNT.

Investigations on 1Pd/5Sm-CNT, which is selected as the best catalyst in solvent-free oxidation of benzyl alcohol, were carried out in detail. Time course of 1Pd/5Sm-CNT in target reaction was detected periodically as shown in Figure 5.11. The conversion of benzyl alcohol monotonically increases with the passage of reaction time followed by a monotone decrease of the qTOF value. During the reaction time course, more and more substrate is converted, while due to the decrease of the concentration of substrate, the reaction rate becomes slower which is reflected as the decline in qTOF value. The selectivity toward benzaldehyde is 82.5% at the first 0.5 h. This low selectivity is caused by the high selectivity toward toluene from hydrogenolysis reaction of the C-O bond in benzyl alcohol with the residual H₂ absorbed on Pd from the dehydrogenation reaction. This is in consistence with the mechanism reported by Keresszegi et al. that the dehydrogenation reaction of benzyl alcohol initially exists whether at the absence of molecular oxygen or not [45]. The coproduct H₂ from dehydrogenation reaction is subsequently consumed (1) in the hydrogenolysis of benzyl alcohol to form toluene; and (2) in the oxidation reaction by O₂, which are two parallel competitive reactions. Evidently, O₂ is a much superior hydrogen acceptor than benzyl alcohol, consuming almost all the H₂ and suppressing the extent of hydrogenolysis reaction. With the reaction time going on, more benzaldehyde is formed and partially further oxidized to benzoic acid, which explains the decrease of selectivity toward benzaldehyde after 1 h.

Figure 5.11 Time course of 1Pd/5Sm-CNT catalyst for aerobic oxidation of benzyl alcohol (benzyl alcohol/Pd = 500 mol/g; O₂ flow rate, 20 mL/min; temperature, 160 °C; stirring rate, 1200 rpm).

The recyclability is regarded as a vital factor in the evaluation of heterogeneous catalyst in a multiphase reaction. The active phase with poor stability and reusability may leach out during the reaction, and the metallic components producing susceptible byproducts in a reaction might get poisoned, bringing about the loss of catalytic activity for subsequent runs of target reaction. The recyclability of 1Pd/5Sm-CNT in the solvent-free aerobic oxidation of benzyl alcohol using gaseous oxygen has been investigated, as displayed in Figure 5.12. The catalyst was manually recovered after each reaction batch by washing with acetone, drying at 60 °C and recharged in the next reaction batch. The operation was repeated four times and 1Pd/5Sm-CNT was used in five consecutive runs. The conversion, selectivity and qTOF are accompanied by a moderate decrease, which is ascribed to the loss of active surface area of metallic phase. The Pd content after the five

consecutive cycles remains almost the same as the as-prepared catalyst. The Pd content is not detectable by ICP analysis in the filtrate phase after any batch of reaction, indicating that no leaching of Pd occurs during reactions and the immobilization of metal phase on support has been stabilized after the surface-functionalization of Sm_2O_3 . Therefore, the samarium oxide surface-functionalized CNT supported Pd catalysts possess not merely the improved catalytic performance in benzyl alcohol oxidation, but also the superiority in the resistance against deactivation.

Figure 5.12 Recyclability of 1Pd/5Sm-CNT catalyst for solvent-free aerobic oxidation of benzyl alcohol (benzyl alcohol/Pd = 500 mol/g; oxygen flow rate, 20 mL/min; reaction temperature, 160 °C; time, 1 h; stirring speed, 1200 rpm).

5.5 Summary

A series of rare earth oxides functionalized CNT supported Pd catalysts Pd/ LnO_x -CNT (Ln=La, Ce, Sm, Gd, Er, Yb) have been prepared using wet impregnation method

followed with a metal ion adsorption-reduction process. Rare earth oxides functionalities presented great influence on the catalytic performance. The XRD, TEM, HRTEM, ICP, pyridine adsorption FTIR, CV and CO stripping analysis suggested the impact of rare earth oxides functionalities on Pd nanoparticle size, Pd valence status, electron densities, EAS areas, chemistry environment of active phase and synergistic effect from metal-support interactions, along with the impact on catalytic performance for solvent-free selective aerobic oxidation of benzyl alcohol. Sm₂O₃ surface functionalized CNT with an appropriate amount of Sm₂O₃ coverage exhibited the best improvement due to the smallest Pd particle size, enhanced metal-support interactions, appropriate electron donor properties of Sm₂O₃ and improved chemistry environment surrounding Pd nanoparticles. Amount of Sm₂O₃ displayed impact on catalytic performance as well since different Sm₂O₃ content influenced the Pd valence status, electron densities, EAS areas, synergistic effect, metal-support interactions, metal-functionalities contact, Pd nanoparticle size and distribution. Among all the catalysts, 1Pd/5Sm-CNT possessed the highest conversion value of 29.6% whereas 1Pd/10Sm-CNT had the highest qTOF value of 318,760 h⁻¹ and selectivity of 95.7% toward benzaldehyde. 1Pd/5Sm-CNT turns out to be the best candidate standing out from the crowd, considering the yield toward benzaldehyde. This work has been published in *Catalysis Today* (Yan et al. *Catalysis Today*, 2015, <http://dx.doi.org/10.1016/j.cattod.2015.07.021>); reuse in this chapter is under the permission of Elsevier Global Rights Department.

List of abbreviations

CNTs	Carbon nanotubes
CV	Cyclic Voltammetry
EA	Ethyl Acetate
EAS	Electrochemically active surface
FTIR	Fourier Transform Infrared Spectroscopy
ICP	Inductively Coupled Plasma
TEM	Transmission Electron Microscopy
TOF	Turn Over Frequency
XRD	X-Rays Diffraction

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Chapter 6 Surface-functionalized carbon nanosphere for selective oxidation of benzyl alcohol, glycerol and the aldol condensation reactions

Aldehydes, such as benzaldehyde and cinnamaldehyde serve as critical intermediates in industrial and laboratorial organic synthesis as well as the valuable products for antimicrobial, flavors, agrichemicals and pharmaceutical industries. Benzaldehyde is generally produced from the selective oxidation of benzyl alcohol. Besides, benzyl alcohol oxidation reaction plays a paramount role as a laboratorial model aromatic alcohol oxidation for catalytic investigations since benzaldehyde as the main product is a non-enolizable aldehyde, reducing the number of possible side-reactions and avoiding confusion in the explanation of reaction mechanisms [4]. Cinnamaldehyde, as the anti-cancer agent, fungicide as well as flavors for food additives, is formed by the aldol condensation reaction between benzaldehyde and acetaldehyde in acid or base solutions under inert environment without oxidant or reducing agent. Recently, selective oxidation of glycerol has attracted tremendous attention because the expanding regenerative biodiesel production gives rise to a large amount of glycerol as an inexpensive by-product. Glycerol oxidation is a procedure under mild conditions to efficiently transform glycerol into valuable chemicals such as glyceric acid, hydroxypyruvic acid, tartronic acid and dihydroxyacetone [5-8]. Glyceric acid is a vital intermediate to synthesize tartronic acid and mesoxalic acid via further oxidation. Whereas dihydroxyacetone (DHA), recently produced from the inefficient microbial fermentation process, is a critical active ingredient in cosmetic sunless tanning lotions. From the perspective of atom economic concern and environmental issues, significant attention has been focused on developing

heterogeneous catalysts for “greener” reaction processes instead of conventional stoichiometric procedures in homogeneous systems consuming expensive additives and generating liquid waste which contains massive inorganic salts.

Since the first discovery of carbon nanotubes, plenty of efforts have been made to create diversified morphologies of carbon materials, such as hollow coin-like carbons [9], carbon nano-fibers [10], graphene [11], graphene-nanotube fibers [12] and so on. Among these carbon materials with different structures, carbon spheres have attracted tremendous attention because of their important roles in catalyst supports [13-15], adsorbents [16-18] electrode materials for lithium ion batteries [19-21], and template materials for fabricating hollow or core-shell metallic or nonmetallic spheres [22-24]. Various methods have been developed to synthesize carbon spheres including chemical vapor deposition (CVD) [25], pressure carbonization [26], mixed-valence oxide-catalytic carbonization [27], and reduction of carbides with metal catalysis [28]. A “green” synthetic approach free of toxic reagents and organic solvents has been established to transform the readily prepared precursors including glucose [29-31], starch [32] and cyclodextrins solutions [33] to generate carbon spheres by simply using hydrothermal vessels at the temperature ranged from 160 °C to 180 °C. The diameters of carbon nanospheres are influenced by temperature, reaction duration and the concentration of precursor solutions. At constant temperature and reaction time, diameter and size distribution increase with the increase of reaction time and peanut-like or other irregular shapes occur at long reaction duration. High concentration of precursor solution usually leads to large diameters and broader size distributions [30, 34]. Concerning temperature issues, Li et al. reported the diameter decreased when

the temperature increased from 180 °C to 190 °C while broken or irregular shapes of carbon nanospheres appeared at 210 °C using 0.3 M glucose solution [34]. According to the discussion of temperature, reaction time and precursor concentration factors, the diameters and size distribution of carbon nanospheres can be well controlled by controlling these three parameters. The surface of the as-synthesized carbon spheres comprises abundant hydrophilic surface functional groups including C–OH, C=O and –COOH groups which can enable the promising application of carbon spheres for water-treatment adsorbent [16, 35, 36]. Other applications involve the support materials for metal or metal oxides ascribed to the strong adsorbent capacitance of metallic ions [30, 31, 37] as well as the template materials to synthesize hollow or core-shell metal spheres or metal oxide spheres [38, 39].

For carbonaceous materials such as activated carbon, it has been extensively reported that the surface hydrophilicity and adsorption capacity can be modified by treating with acids or bases [40-45]. The surface of CNS is enriched with C–OH and C=O groups, the density of which can be controlled by similar chemical treatment in acid or base solutions. In addition to the pretreatment using acid and base, adding acrylic acid monomer during the hydrothermal synthesis has been reported to prepare the carboxyl-groups-functionalized CNS [35]. Another approach is through the post-synthesis acid treatment, leading to CNS covered with –SO₃H and –COOH functional groups, which have been utilized as the solid-acid catalysts for the hydrolysis of polysaccharides [46]. Nonetheless, literatures reporting the treatment of CNS in order to prepare the solid base catalyst for typical base-catalyzed reactions such as aldol condensation are limited up to now. Several typical base-catalyzed reactions such as

Michael addition, alkylation, isomerization, Knoevenagel, adol and Claisen-Schmidt condensations are commonly used for industrial chemical production of pharmaceuticals, perfumes, flavors, bulk and fine chemicals. Currently, more than 1.5 million tons of bulk chemicals are produced annually through reactions catalyzed by either sodium hydroxide or potassium hydroxide, and the liquid waste has to be neutralized by acids, which accounts about 30% of the overall cost [47]. Thus, the development of less-expensive solid base catalyst is essential for the industrial base-catalyzed reactions. Besides, regarding the strong metal adsorption capacitance of CNS [16] and its flexibility of surface modification, functionalized CNS may serve as excellent catalytic support for metallic nanoparticles.

6.1 Characterization of surface-functionalized carbon nanospheres and their supported catalysts

Figure 6.1 (A) TEM and FESEM observations of the as-synthesized carbon nanospheres (CNS) and (B) nitrogen adsorption-desorption isotherm of carbon nanospheres.

Figure 6.1A demonstrates the TEM and FESEM observations of the as-synthesized CNS sample with good dispersion and relatively uniform diameters ranged from 50 nm to 300 nm, close to the result reported by Song et al. [16]. The hydrothermally synthesized CNS is nonporous attributed to the low specific surface area ($35.5 \text{ m}^2/\text{g}$) and pore volume (0.03 mL/g), similar to the literatures results [16, 29-31]. The extremely low pore volume may be resulted from the inter-particle space [16]. Surface activation of CNS by NaOH solution at room temperature did not make obvious changes in the surface area, pore volume and morphology, which is different from the high-temperature treatment of carbon sphere using solid alkali [50]. Raman spectroscopy was employed to characterize the CNS and functionalized CNS with the results shown in Figure 6.2. The graphitic G-band at 1580 cm^{-1} , is ascribed to the graphite-oriented Raman-active E_{2g} mode [51, 52]. While the disordered carbon-oriented D-band at 1370 cm^{-1} is derived from the structural defect, finite size effect and lattice distortion of carbon spheres [53], which is weak in the native CNS and even weaker in the NaOH activated CNS for observation or integration. Sun et al. reported the CNS was hydrothermally generated in two steps: glucose polymerization and aromatization/carbonization which leads to carbonized core and hydrophilic sugar-polymerized surface [30]. Therefore, Raman results in this study imply that the highly ordered carbonized core occupies the major content of the CNS bulk material and the further CNS activation with alkali solution consumes some of the surface non-carbonized or amorphous species.

Figure 6.2 Raman spectra of CNS, CNS-0.1OH, CNS-0.3OH, CNS-0.5OH, CNS-0.7OH, CNS-1OH, CNS-3OH and CNS-5OH

Figure 6.3 FTIR spectra of CNS, CNS-0.1OH, CNS-0.3OH, CNS-0.5OH CNS-0.7OH, CNS-1OH, CNS-3OH and CNS-5OH

The most significant alternation occurred in surface properties rather than in the bulk properties. In Figure 6.3, the FTIR spectra of CNS, CNS-0.1OH, CNS-0.3OH,

CNS-0.5OH, CNS-0.7OH, CNS-1OH, CNS-3OH and CNS-5OH are displayed. The strong adsorption band from 3100 to 3400 cm^{-1} indicates the O–H stretching vibration which may be overlapped by the O–H stretching vibration of water molecules, implying the strong hydrophilicity to adsorb water. The band centered at 1700 cm^{-1} is attributed to the stretching vibration of C=O in lactone groups [54], aldehyde groups [55] or carboxyl groups [35, 56-59]. The band at 1600 cm^{-1} indicates the C=C stretching vibrations, while the mild peaks at around 2923 cm^{-1} imply the presence of aliphatic –CH, with the bands at 1023 cm^{-1} for C–OH stretching vibration and 1367 cm^{-1} for the symmetric stretching vibration of –COO^- , the deprotonated carboxylate group [16]. There is an obvious increase of the strength of the stretching vibrational band of deprotonated carboxylate group –COO^- at 1367 cm^{-1} as the alkali concentration increases. These are because of the reactions occurred during the treatment process described as follows. The NaOH solution can trigger the hydrolysis of lactone and deprotonate the carboxyl groups, which are consistently used to explain the decrease in the 1700 cm^{-1} band strength of the lactone C=O stretching vibration and the increase in the strength of the 1367 cm^{-1} peak derived from the deprotonated carboxylate group –COO^- as the base concentration increases [42, 45, 60]. In addition, Cannizzaro reaction, the base-induced disproportionation reaction of an aldehyde without alpha hydrogen, such as the aldehyde groups on aromatic rings formed by the carbonization step, would occur to simultaneously generate hydroxyl and deprotonated carboxylate groups in alkali solutions [61]. Generally, the higher the alkali concentration, the more deprotonated –COO^- groups are generated.

The XPS core level spectra of O 1s has been monitored and deconvoluted as demonstrated in Fig. 6.4. The O 1s XPS spectra discloses the significant escalation in the value of C=O/C-O fraction: 0.7, 2.4, 4.2, 6.6 and 8.4 for Pd/CNS, Pd/CNS-0.1OH, Pd/CNS-0.3OH, Pd/CNS-0.5OH and Pd/CNS-0.7OH respectively, with C=O band within the scale of 531.5-532.5 eV, C-O band within the scale of 533-536 eV and the lattice oxygen within the scale of 529.8-530.1 eV [49]. Since the two O atoms are equivalent in the deprotonated COO^- group attributed to the $p-\pi$ conjugation structure, one COO^- group doubles the strength of C=O peak and the emergence of COO^- shifts the C=O band toward higher binding energy. The significant increase of the C=O/C-O fraction with the increase of alkali concentration used to functionalize CNS further substantiates the occurrence of the alkali deprotonating carboxyl groups and hydrolysis reaction of lactone to form hydroxyl as well as the deprotonated COO^- groups. In consistent with the FTIR results, the higher the alkali concentration generates more deprotonated COO^- groups.

Figure 6.4 XPS spectra of O *1s* in Pd/CNS, Pd/CNS-0.1OH, Pd/CNS-0.3OH, Pd/CNS-0.5OH and Pd/CNS-0.7OH catalysts.

Zeta potential is the potential difference of the interfacial double layer, the stationary layer of fluid attached to the dispersed particle and a point in the bulk fluid medium. It is proportional to the charge density on sample surface. As shown in Table 6.1 and 6.2, the zeta potential (measured with 12.5 mg of samples dispersed in 25 mL

of pH buffer solution ($\text{pH}=7.00\pm0.02$) using a zeta potential analyzer BIC PALS) of CNS, CNS-0.1OH, CNS-0.3OH, CNS-0.5OH, CNS-0.7OH, CNS-1OH, CNS-3OH and CNS-5OH dispersed in deionized water have been measured with the results being -26.8 mV, -37.6 mV, -41.8 mV, -43.9 mV, -46.4 mV, -47.9 mV, -50.9 mV and -52.3 mV, respectively. The lower zeta potential of alkali activated CNS with more negatively charged surface was consistently explained by the presence of the above two base-induced lactone hydrolysis and carboxyl groups deprotonating reactions, which giving rise to the negatively charged -COO^- surface functional groups [62, 63]. Meanwhile, the lower zeta potential indicates higher surface basicity which may require more protons to neutralize. In Table 6.1 and 6.2, the pH values of these samples dispersed in distilled water have also been measured for comparison, results as 6.6, 9.0, 9.2, 9.3, 9.6, 9.8, 10.1 and 10.7 for CNS, CNS-0.1OH, CNS-0.3OH, CNS-0.5OH, CNS-0.7OH, CNS-1OH, CNS-3OH and CNS-5OH respectively. The surface of native CNS is mildly acidic because the hydrothermal synthesis of CNS from glucose generates some carboxyl groups which are acidic. These above pH results are in line with the zeta potential results, further verifying the increased surface basicity and increased amount of -COO^- surface functional groups generated by the above two reactions induced by the increased concentration of sodium hydroxide solution.

XRD patterns and TEM observations have been employed to characterize the metallic Pd nanoparticles supported on CNS and functionalized CNS. Figure 6.5 demonstrates the XRD patterns of CNS, Pd/CNS, Pd/CNS-0.1OH, Pd/CNS-0.3OH, Pd/CNS-0.5OH and Pd/CNS-0.7OH. The diffraction peaks at 40.00° and 46.50° are respectively derived from the (1 1 1) and (0 0 2) planes in the face centered cubic

(FCC) crystal structure of palladium [4]. The strength of Pd characteristic diffraction peaks are diminished with the increase of the alkali concentration. Meanwhile, the increase in the full width at half maximum (FWHM) with the decrease of peak strength indicates the reduced Pd particle size on the CNS pretreated with higher concentration of NaOH according to the Scherrer equation [64, 65]. Highly dispersed and smaller-sized Pd nanoparticles were achieved by the surface functionalized CNS which has been further substantiated by TEM observations as displayed in Figure 6.6. The average sizes with standard deviations of Pd/CNS, Pd/CNS-0.1OH, Pd/CNS-0.3OH, Pd/CNS-0.5OH and Pd/CNS-0.7OH are 7.5 ± 1.5 nm, 6.1 ± 2.6 nm, 5.1 ± 1.9 nm, 4.2 ± 2.3 nm and 2.7 ± 1.5 nm respectively, which are in accordance with the XRD results. The high dispersion was obtained owing to the strong surface hydrophilicity of CNS. Further surface functionalization using alkali solutions with increased concentration can orderly change the composition of surface functional groups, decreasing the amount of lactone or aldehyde groups and increasing the amount of deprotonated carboxylate groups which can subsequently increase the surface hydrophilicity and more surface negatively charged sites. Therefore, the improved hydrophilicity favors the adsorption of Pd^{2+} ions while the negatively charged surface related to the deprotonated carboxylate groups facilitates the electrostatic attraction of the positively charged metallic ions as well as the hydrolysis of Pd^{2+} ions for its immobilization onto the support surface, all of which significantly facilitate the formation of smaller Pd nanoparticles evenly dispersed on the functionalized CNS support.

Figure 6.5 XRD patterns of CNS, Pd/CNS, Pd/CNS-0.1OH, Pd/CNS-0.3OH, Pd/CNS-0.5OH and Pd/CNS-0.7OH.

Figure 6.6 TEM images and Pd particle size distribution histograms of (A) Pd/CNS; (B) Pd/CNS-0.1OH; (C) Pd/CNS-0.3OH; (D) Pd/CNS-0.5OH and (E) Pd/CNS-0.7OH.

The adsorption capacity of Pd species differed among all these catalysts, illustrated by the ICP results displayed in Table 6.1. The native CNS without alkali activation exhibits the weakest adsorption strength of Pd species, with the Pd content

on Pd/CNS catalyst being 1.16 wt.% while 1.18 wt.%, 1.24 wt.%, 1.29 wt.% and 1.25 wt.% for Pd/CNS-0.1OH, Pd/CNS-0.3OH, Pd/CNS-0.5OH and Pd/CNS-0.7OH respectively. The alkali solution activation obviously promotes the metallic ion adsorption capacitance of CNS due to the generation of abundant hydrophilic groups including the negatively charged deprotonated -COO^- group. The CNS-0.5OH displays the highest adsorption capacity of Pd species which is in agreement with the study of adsorption kinetics explained by Song et al. [16].

The XPS core level spectra of Pd 3d have been monitored and deconvoluted as demonstrated in Figure 6.7. The Pd 3d peaks are derived from the Pd 3d_{3/2}, Pd 3d_{5/2} orbitals and each of the two orbitals can be deconvoluted into two peaks because of the presence of two chemical states, the metallic Pd⁰ state and cationic Pd²⁺ state [4]. The fractions of Pd⁰ (Pd⁰/Pd) in Pd/CNS, Pd/CNS-0.1OH, Pd/CNS-0.3OH, Pd/CNS-0.5OH and Pd/CNS-0.7OH catalysts are 36.4 %, 47.9 %, 56.8 %, 65.1 % and 55.9 % respectively. Surface modification by alkali activation favors the generation of more reduction state Pd. This effect can be strengthened with the increase in alkali concentration until it reaches 0.5 M. However, further increase the alkali concentration to 0.7 M goes the other way around. The negatively charged surface can somehow augment the electron density of Pd nanoparticles. Besides, during the Pd reduction process, proper surface basicity of functionalized CNS enhances the reducibility of the reducing agent $[\text{BH}_4]^-$ which would otherwise easily react with the acidic H⁺ in aqueous medium. Nevertheless, highly negative surface may repel the reductive $[\text{BH}_4]^-$ anions from getting close to the Pd²⁺ adsorbed on the functionalized CNS surface and thus hamper the reduction process of Pd²⁺ to form Pd⁰. Other

explanations include the stronger adsorption of O₂ over the smaller Pd nanoparticles (2.7 nm) may somehow undermine the Pd electron densities on the Pd/CNS-0.7OH catalyst [66]. Moreover, owing to the rich surface functional groups of –CH₂OH and –COO[–] generated by the 0.5M NaOH activation, direct redox adsorption of Pd²⁺ ions converted to Pd⁰ may also occur on functionalized CNS-0.5OH [16]. Therefore, the Pd/CNS-0.5OH catalyst possesses the highest Pd⁰/Pd of 65.1%.

Figure 6.7 XPS spectra of Pd 3d in Pd/CNS, Pd/CNS-0.1OH, Pd/CNS-0.3OH, Pd/CNS-0.5OH and Pd/CNS-0.7OH catalysts.

6.2 Surface-functionalized carbon nanospheres for aldol condensation reaction to synthesize cinnamaldehyde

Table 6.1 Zeta potential, pH and Catalytic results of aldol condensation over CNS-1OH, CNS-3OH and CNS-5OH.^a

Entry	Catalyst	ζ Potential	ζ Potential	pH	Conversion (%)	Yield (%)			Carbon balance of ^c
		(mV) before reaction	(mV) after reaction			cis- + trans-	cis- + trans-	cis- + trans-	
1	^a CNS-1OH	-47.9	-46.5	9.8	23.7	23.7	0	0	97.6 %
2	CNS-3OH	-50.9	-49.1	10.1	32.0	32.0	0	0	97.7 %
3	CNS-5OH	-52.3	-51.4	10.7	28.1	28.1	0	0	97.4 %
4	^b NaOH-			12.0	41.9	41.2	0.7	0	96.6 %
5	NaOH-0.05M			12.7	68.3	66.7	1.6	0	95.8 %
6	NaOH-0.07M			12.8	69.5	67.3	2.1	0.1	95.3 %
7	NaOH-0.1M			13.0	74.6	71.1	3.3	0.2	93.1 %
8	NaOH-0.2M			13.3	79.5	69.0	9.4	1.1	92.9 %
9	NaOH-0.5M			13.7	87.2	68.7	16.5	2.0	91.5 %
10	NaOH-0.7M			13.8	79.8	65.0	11.8	3.0	90.1 %

^a Reaction conditions: CNS, 0.1 g; H₂O, 10 mL; ethanol, 5 mL; benzaldehyde, 1 mL; acetaldehyde, 1 mL; inert nitrogen atmosphere; stirring rate, 1200 rpm; temperature, 25 °C; time, 5 h.

^b Control experiment conditions: NaOH solution (0.01M, 0.05 M, 0.07 M, 0.1 M, 0.2 M, 0.5 M or 0.7M), 25 mL; ethanol, 5 mL; benzaldehyde, 1 mL; acetaldehyde, 1 mL; nitrogen atmosphere; temperature, 25 °C; time, 5 h.

^c Carbon balance was measured by equation:
$$\frac{(\text{GC peak area of product} + \text{reactant residual})/(\text{corresponding inert standard peak area})}{(\text{GC peak area of reactant before reaction})/(\text{corresponding inert standard peak area})}$$
 using tetradecane (C14) used as the inert standard.

Table 6.2 Effect of temperature on catalytic results of aldol condensation over CNS-3OH.^a

Entry	Temperature (°C)	Conversion (%)	Yield (%)			Carbon balance of ^b
			cis- + trans-	cis- + trans-	cis- + trans-	
1	20	25.7	25.7	0	0	98.3 %
2	25	32.0	32.0	0	0	97.7 %
3	30	32.5	32.5	0	0	97.6 %
4	35	33.2	32.1	1.1	0	97.3 %
5	40	33.9	31.8	2.1	0	97.3 %

^a Reaction conditions: CNS-3OH, 0.1 g; H₂O, 25 mL; ethanol, 5 mL; benzaldehyde, 1 mL; acetaldehyde, 1 mL; nitrogen atmosphere; stirring rate, 1200 rpm; time, 5 h.

^b Carbon balance was measured by equation: $\frac{(\text{GC peak area of product} + \text{reactant residual})/(\text{corresponding inert standard peak area})}{(\text{GC peak area of reactant before reaction})/(\text{corresponding inert standard peak area})}$ using tetradecane (C14) used as the inert standard.

Aldol condensation reaction is a well-known base-catalyzed reaction under mild physical conditions, widely used for achieving the carbon chain growth in aldehyde molecules. One famous aldol condensation reaction undergoes between benzaldehyde and acetaldehyde to form cinnamaldehyde. The industrial aldol condensation procedures consume millions of tons of alkali owing to which the liquid waste requires be neutralized by acids occupying a large portion of the overall production cost. The surface functionalized CNS was employed to serve as the heterogeneous solid base catalyst in aldol condensation reaction for the continuous production of cinnamaldehyde. As displayed in Table 6.1, the alkali aqueous solution activated CNS is applicable for catalyzing the aldol condensation reaction. The functionalized CNS surface presents the nature of weak base due to the presence of the deprotonated -COO^- group and many other oxygen-containing proton acceptors. The NaOH aqueous solutions were also employed for comparison. They lead to high conversion values but larger extent of side reactions as well. Since the aldol condensation reaction is initiated by the alkali attacking the α -H of aldehyde, the aldehydes with α -H are quite sensitive to strong, steric hindrance-free and highly concentrated alkali solutions. Higher alkali concentration not only enhances the conversion of benzaldehyde but also largely promotes side reactions at the same time. 0.5 M NaOH solution generates the highest conversion of benzaldehyde while 0.1 M NaOH solution leads to the highest yield toward cinnamadehyde. Side reactions seem to be inevitable for the strong base catalyzed aldol condensation reaction. Acetaldehyde was supposed to react with benzaldehyde to form cinnamaldehyde but the cinnamaldehyde can further react with the active acetaldehyde with the presence of strong base. Similarly, carbon chain might be elongated by the subsequent condensation

reaction with acetaldehyde under strong basic environment. In addition, one molecule of acetaldehyde can react with another molecule of acetaldehyde and the products can react with acetaldehyde as well. Likewise, the carbon chain also can be elongated consuming large amount of acetaldehyde and thus hampering the extent of the targeted main reaction. Additionally, the Cannizzaro reaction may occur under strong basic environment where the products (i.e. benzyl alcohol and benzoate) can be dissolved into the aqueous phase, resulting in the loss of carbon balance of benzaldehyde source inside the organic phase and make the carbon balance value much lower than 100%. The main reaction and possible side reactions are listed as follows.

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Figure 6.8 Schematic diagram of the catalyst-determining mechanism of aldol condensation reaction catalyzed by functionalized CNS activated with alkali aqueous solution.

Although conversions of the functionalized CNS are relatively lower, they significantly reduced the types and extents of side reactions because of their larger steric hindrance, slower motion speed compared to OH^- ions, more moderate basicity and the

highly negatively charged surface. Besides, the carbon balance issues of benzaldehyde using functionalized CNS are much better than those using sodium hydroxide. These benzaldehyde carbon balance values are still lower than 100% indicating the possible loss of reactant or products either in aqueous phase or by the firm adsorption on the CNS surface. The larger steric hindrance, slower motion speed and the more moderate basicity make the solid base attack acetaldehyde at slower rate and therefore averting the rapid emergence of side reactions. Moreover, the negatively charged CNS surface plays a paramount role in this highly selective aldol condensation reaction to form cinnamaldehyde according to the mechanism as shown in Figure 6.8. The negatively charged CNS electrostatically attracted the partially positively charged (δ^+) carbonyl carbon end of the nearby aldehyde molecules. The strength of the partially positive charge (δ^+) on carbonyl carbons of aldehydes decreases in the order as below, because of the fact that the presence of larger π electron conjugation system can diminish the strength of positive charge on carbonyl group.

Unless the randomly fast moving acetaldehyde has the possible chance to provide its α -H for attacking by the surface basic sites. Upon the formation of carbon anion intermediate after several electron transferring steps as shown in Figure 6.8, the carbon anion intermediate instantly attacked the nearby carbonyl groups readily closely located beside the CNS surface. It means the carbon anion intermediate of acetaldehyde can react with either benzaldehyde or acetaldehyde, and the reaction between two acetaldehydes consumes the available acetaldehyde hampering the objective conversion of

benzaldehyde. Since the partially positive charge (δ^+) of the carbonyl group on cinnamaldehyde is even weaker than acetaldehyde or benzaldehyde, implying the cinnamaldehyde molecules may get far away from the negatively charged CNS surface, the chance of acetaldehyde reacting with cinnamaldehyde is significantly lower. That is why the selectivity toward cinnamaldehyde from benzaldehyde is 100% over CNS-1OH, CNS-3OH and CNS-5OH catalysts without further aldol condensation reactions elongating the carbon chain of aromatic rings, which, are quite normally observed in the cases using NaOH solutions. Even though the reaction time is prolonged to 10 h, the yields toward cinnamaldehyde are equal or close to conversion of benzaldehyde which means the selectivity values toward cinnamaldehyde are equal or close to 100% as shown by the conversion-time curve combined with the selectivity-time curve plotted in Figure 6.9. The CNS-5OH catalyst displayed a lower conversion in contrast to CNS-3OH because the stronger surface negative charge possesses the stronger electrostatic attraction toward the partially positively charged (δ^+) carbonyl groups, enhancing the steric hindrance effect and hindering the attacking rate by the carbon anions of acetaldehyde molecules. Therefore, the properly functionalized CNS-3OH presents the highest conversion among CNS-1OH, CNS-3OH and CNS-5OH catalysts and it was selected as the optimal base catalyst in aldol condensation reaction for further investigation.

Figure 6.9 The conversion-time and selectivity-time curves of aldol condensation reaction to form cinnamaldehyde under reaction condition: functionalized CNS, 0.1 g; H₂O, 10 mL; ethanol, 5 mL; benzaldehyde, 1 mL; acetaldehyde, 1 mL; inert nitrogen atmosphere; stirring rate, 1200 rpm; temperature, 30 °C.

The effect of temperature has been investigated and results are summarized in Table 6.2. The reaction undergoes five runs at 20 °C, 25 °C, 30 °C, 35 °C and 40 °C respectively. Side reactions are sensitive to temperature in this system because the electrostatic attraction and steric hindrance control which can determine the high selectivity can be undermined by the temperature dependent molecular random motions. High temperature drastically increased the random motion speed of molecules which can break loose from the electrostatic attraction force as well as the steric hindrance control and subsequently react with whatever they can react with, increasing the overall conversion at the sacrifice

of selectivity or yield toward the objective product. It means lower temperature ensures higher selectivity however it is always accompanied by lower conversion and reaction activity at the same time. Therefore, the optimized selection of reaction temperature must be a specific value in between these two extremes. In this study, 30 °C was considered as the optimized reaction temperature for aldol condensation reaction to form cinnamaldehyde using CNS-3OH because of the highest yield and the 100% selectivity.

Figure 6.10 Recyclability of CNS-3OH catalyst for aldol condensation reaction to form cinnamaldehyde under reaction conditions: CNS-3OH, 0.1 g; H₂O, 10 mL; ethanol, 5 mL; benzaldehyde, 1 mL; acetaldehyde, 1 mL; inert nitrogen atmosphere; stirring rate, 1200 rpm; temperature, 30 °C.

Recyclability was investigated as well for the assessment of CNS-3OH catalyst which was reused in five consecutive runs of aldol condensation reaction, results shown in Figure 6.10. The catalyst was recovered via rinsing with ethanol and drying at 40 °C under vacuum followed by the reuse in the next batch of reaction. The loss of conversion, yield and selectivity is insignificant during the first three cycles of reactions, implying the stable catalytic performance of CNS-3OH as a solid base catalyst for the first 3 runs of aldol condensation reaction. However, the diminished conversion, yield and selectivity in the fourth and fifth cycles of reaction indicate the damage of surface basicity and the loss of surface negative charge. The adsorption of some positively charged or acidic molecules which can partly neutralize the surface negative charge or surface basicity may deteriorate the catalytic performance.

6.3 Surface-functionalized carbon nanospheres supported Pd catalysts for benzyl alcohol selective oxidation reaction

Solvent-free selective oxidation of benzyl alcohol using gaseous oxygen was employed as a probe reaction to disclose the effect of alkali activation of CNS on the catalytic performance of Pd nanoparticles, with the results displayed in Table 6.3. A dramatic increase in the selectivity toward benzaldehyde was observed using Pd supported on CNS activated by increased alkali concentration which was in agreement with the conclusion drawn by Enache that the acidic nature of catalytic support leads to enhanced byproduct formation [67]. In another word, the enhanced surface basicity facilitates the inhibition of side reactions which commonly form toluene or benzoic acid. The basic catalyst support and hydrophilic surface favor the high dispersion and formation of small sized Pd nanoparticles [4]. According to the

TEM observation shown in Figure 6.6, the particle size of palladium gradually decreases with the increase of alkali concentration, which is associated with the increased surface basicity and hydrophilicity. However, when the Pd particles are as small as 2.7 nm in Pd/CNS-0.7OH, the catalytic activity is not as good as the 4.2 nm sized Pd nanoparticles in Pd/CNS-0.5OH. Zhang et al emphasized the importance of the coordinatively unsaturated sites, such as the edge or corner atoms on the catalytic particle surface for the oxidative dehydrogenation of benzyl alcohol. Besides, the terrace Pd atoms also play a crucial role in benzyl alcohol oxidation reaction. To be precise, the adsorption of benzyl alcohol which requires terrace atoms on Pd nanoparticles is an important step for its subsequent activation and conversion. Meanwhile, the β -H cleavage (i.e., C–H bond activation) requires the edge and corner atoms. Further computation results exhibit that the Pd nanoparticles sized from 3.6 to 4.3 nm possess the highest TOF, corresponding to the fraction value of (number of terrace atoms)/(number of edge and corner atoms) ranging from 2.3 to 3.1. In conclusion, the optimum Pd particle size is around 4 nm which possesses an optimum ratio of terrace to (edge and corner) Pd atoms for the benzyl alcohol adsorption followed by the β -H cleavage [66]. These discussions can be used to explain the result that the 4.2 nm sized Pd particles on the Pd/CNS-0.5OH catalyst demonstrated the highest catalytic activity for selective oxidation of benzyl alcohol, from the perspective of the size effect on the catalytically active phases. In addition, the highest electron density of Pd nanoparticles on the Pd/CNS-0.5OH catalyst inspected by XPS spectra may contribute to its catalytic performance for the oxidative dehydrogenation of benzyl alcohol as well because the high electron density, which is

proportional to the Pd⁰/Pd fraction, favors the electron transfer efficiency and the adsorption of oxygen, a sort of electrophilic reagent. Grunwaldt et al. reported that the metallic palladium (Pd⁰) is more active catalytic phase for aerobic oxidation of benzyl alcohol than the palladium oxide because the metallic palladium is related to rapid access to adsorbed oxygen [68]. Additionally, Zhu et al. suggested that the surface oxygen-containing species on catalyst support are useful for oxygen activation [69]. Therefore, the Pd/CNS-0.5OH catalyst displays the best catalytic performance through attaining a well-balanced situation between the electronic effect and the oxygen activation effect. In contrast, the catalytic activity of Pd/CNS-0.7OH is relatively lower due to the smallest Pd particle size of 2.7 nm, which is inferior to the size around 4 nm possessing the best balance of reactant adsorption over terrace atoms and β-H cleavage over edge or corner atoms. On the other hand, the stronger adsorption of O₂ over Pd particles as small as 2.7 nm and the relatively lower electron density (Pd⁰/Pd as 55.9%) can impede the efficiency of the rapid electron transfer during the oxidation of benzyl alcohol. The carbon balances have been calculated according to the equation with tetradecane (C₁₄) used as the inert standard:

$$\text{carbon balance} = \frac{\left[\frac{(\text{GC peak area of product} + \text{reactant residual})}{(\text{corresponding tetradecane peak area after reaction})} \right]}{\left[\frac{(\text{GC peak area of reactant before reaction})}{(\text{corresponding tetradecane peak area before reaction})} \right]} \times 100\%$$

The results of carbon balance are usually smaller than 100% due to some systematic errors and the loss of reactants or products converted into volatile molecules such as CO₂ or CO. The basic surface of catalyst support may also adsorb trace amount of acidic byproducts. Since the carbon balance values are close to 100%,

the carbon loss can be neglected and thus the obtained catalytic results are reliable.

Figure 6.11 The conversion, q_{TOF} and selectivity plot as functions of time in benzyl alcohol oxidation reaction. Reaction conditions: catalyst, 10 mg; benzyl alcohol, 50 mmol; temperature, 120 °C; O_2 flow rate, 20 mL min⁻¹; time, 10 h; stirring rate, 1200 rpm.

Table 6.3 Zeta potential, pH and Catalytic results of benzyl alcohol oxidation over Pd/CNS, Pd/CNS-0.1OH, Pd/CNS-0.3OH, Pd/CNS-0.5OH and Pd/ CNS-0.7OH catalysts.^a

Entry	Catalyst	ζ Potential of support (mV)	pH of support	Pd ^b (wt.%)	Conversion (%)	Selectivity (%)			qTOF ^c (h ⁻¹)	Carbon balance ^d

1	Pd/CNS	-26.8	6.6	1.16	11.0	76.2	23.5	0.3	5,046	98.8 %
2	Pd/CNS-0.1OH	-37.6	9.0	1.18	14.4	97.2	2.8	0	6,493	98.2 %
3	Pd/CNS-0.3OH	-41.8	9.2	1.24	17.3	98.4	1.6	0	7,424	97.2 %
4	Pd/CNS-0.5OH	-43.9	9.3	1.29	22.9	100	0	0	9,446	97.3 %
5	Pd/CNS-0.7OH	-46.4	9.6	1.25	18.5	100	0	0	7,875	97.9 %

^a Reaction conditions: catalyst, 10mg; benzyl alcohol, 50mmol; O₂, 20mL/min; stirring rate, 1200 rpm; temperature, 120°C; time, 1h.

^b Metal content was obtained by ICP.

^c qTOF has been derived from the Pd metal content analyzed by ICP.

^d Carbon balance was measured by equation:
$$\frac{(\text{GC peak area of product} + \text{reactant residual})/(\text{corresponding inert standard peak area})}{(\text{GC peak area of reactant before reaction})/(\text{corresponding inert standard peak area})}$$
 using tetradecane (C14) used as the inert standard.

Figure 6.11 exhibits the reaction time dependences of each catalyst performance in selective oxidation of benzyl alcohol. The onset reaction rates ranged in the order of Pd/CNS-0.5OH > Pd/CNS-0.3OH > Pd/CNS-0.7OH > Pd/CNS-0.1OH > Pd/CNS. All the catalysts possess the gradually undermined catalytic performances which are associated with the catalytic activity (qTOF) proportional to decreasing slope of the conversion-time curve. Such deactivation is resulted from either the coverage of the adsorbed species on Pd surface [70] or the aggregation of Pd particles due to over-oxidation [71]. The hydrocarbon adsorbed on Pd active sites hampers the adsorption of reactants and meanwhile the over-oxidation favors the formation of Pd-O-Pd structure, resulting in larger clusters of particles [49]. Such effects are more apparent for Pd/CNS-0.5OH and Pd/CNS-0.7OH catalysts which demonstrate the faster drop of catalytic activities. Nonetheless, Pd/CNS demonstrates different catalytic activity trend along with reaction time. It initially shows lowest conversion and qTOF resulted from the lowest concentration of Pd⁰/Pd indicating the lowest electron density as well as the weak electron transfer efficiency. The increase of catalytic activity during the first four hours can be correlated to the valence transition of Pd upon the adsorption of alcohol molecules. Such period is called catalyst activation period when the adsorbed alcohol molecules serve as the reducing agent chemically transforming the Pd²⁺ into Pd⁰ state [72].

The recyclability is regarded as a fundamental factor in the assessment of a heterogeneous catalyst in multiphase system. The less stable active phase with poor recyclability leaches out during the reaction process and subsequently leads to the active homogeneous catalyst at the sacrifice of losing catalytic activity for

consecutive batches of reaction. The recyclability of Pd/CNS-0.5OH in selective oxidation of benzyl alcohol has been examined. The catalyst was recovered via rinsing with ethanol and drying at 50 °C under vacuum condition followed by the reuse in the next batch of reaction. Figure 6.12 demonstrates the recyclability of Pd/CNS-0.5OH for five consecutive batches of reaction cycles. The loss of catalytic activity and selectivity is minor, implying that the loss of active sites during recovery is moderate. The Pd content after the five sequential batches of reaction is close to the freshly produced catalyst without obvious leaching due to the strong metal-support interaction after modifying the CNS surfaces. Strong adsorption capacity and efficiency of metal particles by 0.5 M NaOH activated CNS were also reported by Song et al [16]. Therefore, the 0.5 M NaOH activated CNS supported Pd catalyst has improved the catalytic performance as well as the anti-deactivation capability.

Figure 6.12 Recyclability of Pd/CNS-0.5OH catalyst for selective solvent free oxidation of benzyl alcohol under reaction conditions: catalyst, 10 mg; benzyl alcohol, 50 mmol; temperature, 120 °C; O₂ flow rate, 20 mL min⁻¹; time, 1 h; stirring rate, 1200 rpm.

6.4 Surface-functionalized carbon nanospheres supported Pd for selective glycerol oxidation reaction

Table 6.4 The catalytic performance of the catalysts below for aerobic oxidation of glycerol.^a

Entry	Catalyst	Pd ^b (wt.%)	Conversion (%)	Selectivity (%)									qTOF (h ⁻¹) ^c	Carbon balance ^d
				DHA	GLYA	GLYHD	GLYCA	MOXA	OXA	TARAC	GLYOA	HPYA		
1	Pd/CNS	1.16	13.7	7.5	28.8	1.9	2.6	13.3	33.1	2.4	2.1	8.3	109.3	97.6 %
2	Pd/CNS-0.1OH	1.18	17.5	5.6	23.1	1.2	5.4	25.7	30.1	4.4	1.1	3.4	137.2	97.4 %
3	Pd/CNS-0.3OH	1.24	21.4	3.9	22.6	0.9	6.2	27.6	29.0	7.0	0.0	2.8	159.7	96.8 %
4	Pd/CNS-0.5OH	1.29	20.8	3.2	17.6	0.0	10.0	30.3	28.1	8.6	0.0	2.2	149.2	96.3 %
5	Pd/CNS-0.7OH	1.25	18.3	2.3	16.2	0.0	11.4	31.2	26.8	10.1	0.0	2.0	135.5	96.2 %

^a Reaction conditions: 20 mL glycerol aqueous solution (10 wt.%), 50 mg catalyst, O₂ flow rate at 150 mL/min, stirring rate, 1200 rpm; temperature, 80 °C; time, 5 h.

^b Pd metal contents have been analyzed by ICP.

^c $q\text{TOF} = (\text{number of glycerol molecules converted}) / (\text{number of Pd atoms}) / (\text{reaction time, h})$.

^d Carbon balance = the total yield toward DHA, GLYA, GLYHD, GLYCA, MOXA, OXA, TARAC, GLYOA and HPYA. And other byproducts such as CO, CO₂ and HCHO have been detected in gas effluent.

Biomass is a renewable resource of fuels and chemicals in bio-refineries where a large amount of inexpensive glycerol has been generated as a by-product [6]. The efficient processes transforming glycerol into valuable chemicals via oxidation, dehydration, hydrogenolysis, esterification or polymerization are in great demand. Particularly, oxidation using gaseous oxygen is an attractive approach of realizing the transformation since oxygen is readily available and inexpensive and consequently produces only the amicable byproduct, water [73]. As shown in Table 6.4, Pd/CNS, Pd/CNS-0.1OH, Pd/CNS-0.3OH, Pd/CNS-0.5OH and Pd/CNS-0.7OH catalysts have been utilized to catalyze the aerobic oxidation of glycerol to form possible products such as 1,3-dihydroxyacetone (DHA), glyceric acid (GLYA), glyceraldehyde (GLYHD), glycolic acid (GLYCA), mesoxalic acid (MOXA), oxalic acid (OXA), tartronic acid (TARAC), glyoxylic acid (GLYOA) and hydroxypyruvic acid (HYPA), among all of which the high-value products are DHA, GLYA, TARAC and HYPA [5-8]. With the increase in concentration of alkali used to activate CNS, the conversion of glycerol was improved at first and then decreased, with Pd/CNS-0.3OH being the most active catalyst possessing the q_{TOF} of 159.7 h^{-1} . It has been evidenced that base concentration significantly impacts the reaction rate of glycerol oxidation where no catalytic activity was observed without base addition and the increasing base concentration leads to apparently improved conversion of glycerol [74]. It means, in a base-free reactant phase, surface basicity of the heterogeneous catalyst support can facilitate the enhancement of catalytic activity for glycerol conversion. Hence the catalytic activity increases in the order of $\text{Pd/CNS} < \text{Pd/CNS-0.1OH} < \text{Pd/CNS-0.3OH}$. Nonetheless, different from the cases where the base is homogeneously

dissolved in glycerol aqueous solution, the basic surface of solid catalyst support strongly adsorbs the acidic molecules from abundant acid products and block the exposure of metallic active phase. Therefore, the catalytic activity decreases in the order of Pd/CNS-0.3OH > Pd/CNS-0.5OH > Pd/CNS-0.7OH. Moreover, the size effect is a critical factor as well. As the rule of thumb, larger metal particles are accompanied with smaller catalytically active surface exposed to reactant whereas the smaller metal particles have larger contact area with the reactant molecules. It doesn't mean the smaller the better in this reaction, considering the adsorbed acidic molecules which may easily block the exposure of active site surface of the smaller Pd nanoparticles. Consequently, the size effect and surface basicity effect codetermined the Pd/CNS-0.3OH to be the most active catalyst for aerobic oxidation of glycerol.

The selectivity toward DHA obviously decreases in the order of Pd/CNS > Pd/CNS-0.1OH > Pd/CNS-0.3OH > Pd/CNS-0.5OH > Pd/CNS-0.7OH because DHA molecules are instable under conditions of high pH [74]. In particular, the oxidation of the secondary OH group in glycerol molecules turns out to be favored under acidic environment [74-77], but the stronger acidic environment hampers catalytic activity that glycerol oxidation reaction may stop at a pH as low as 3 [74]. In this study, Pd/CNS possesses the best selectivity toward DHA because of its lowest pH. The glyceraldehyde is instable and sensitive to basic environment as well with its selectivity inevitably diminished as the surface basicity enhances. Since both the DHA and glyceraldehyde can interconvert [74], the same trend of selectivity change is understandable. On the contrary, selectivity toward mesoxalic acid (MOXA) escalates significantly along with either the enhanced surface basicity or the

diminished size of Pd nanoparticles, accompanied by the apparently decreased selectivity toward oxalic acid (OXA) which is the most largely produced valueless byproduct. Additionally, the selectivity toward tartronic acid (TARAC) was improved along with either the enhanced surface basicity or the diminished size of Pd nanoparticles. Accordingly, by controlling both of the surface amphoteric property and diameters of nanoparticles, the selectivity or yield of specifically targeted valuable product can be controlled.

Figure 6.13 Time course of the glycerol oxidation over Pd/CNS, Pd/CNS-0.3OH and Pd/CNS-0.7OH catalysts under reaction condition: 20 mL glycerol aqueous solution (10

wt.%), 50 mg catalyst, O₂ flow rate at 150 mL/min, stirring rate, 1200 rpm; temperature, 80 °C.

Figure 6.13 displays the reaction time dependences of glycerol oxidation over Pd/CNS, Pd/CNS-0.3OH and Pd/CNS-0.7OH catalysts. The conversion gradually increases with decreased reaction rate (i.e., the slope of conversion-time curve) while the selectivity values remain stable only with very minor change over each catalyst. The lowest ultimate conversion of glycerol catalyzed by Pd/CNS is attributed to the lowest surface basicity (pH) of catalyst support [74], which is in agreement with previous results. Drastically diminished slope of the conversion-time curve in glycerol oxidation catalyzed by Pd/CNS-0.7OH implies the apparent decrease of reaction rate due to the catalytic deactivation effect, since the Pd nanoparticles as small as 2.7 nm on Pd/CNS-0.7OH can be easily blot out by the strongly adsorbed acidic species. On the other hand, the stable selectivity values infers that in this system the influence of catalyst properties on selectivity distributions may surpass the effect of reaction time and this is in agreement with the results by Hirasawa et al. [73]. Pd/CNS-0.3OH possesses the highest ultimate conversion of glycerol molecules and the decrease in slope of conversion-time curve is not as rapid as either Pd/CNS or Pd/CNS-0.7OH, implying the relatively enhanced anti-deactivation capability.

6.5 Summary

Carbon nanosphere has been hydrothermally synthesized and undergoes activation by alkali aqueous solutions. Both the native and functionalized CNS supported Pd catalysts have been employed for either the selective oxidation of benzyl alcohol or the aerobic oxidation of glycerol to produce targeted products, with the Pd/CNS-

0.5OH demonstrating the highest qTOF of 9,446 h⁻¹ together with the benzaldehyde selectivity of 100% for the former reaction, while the Pd/CNS-0.3OH exhibiting the highest qTOF of 159.7 h⁻¹ for the glycerol oxidation. Surface basicity, electron density and diameters of Pd nanoparticle play paramount roles in these two reactions. In the case of aldol condensation to form cinnamaldehyde using alkali-activated CNS, CNS-3OH displays the optimal conversion, selectivity and yield toward cinnamaldehyde owing to its large steric hindrance, slower motion speed compared to OH⁻ ions, appropriate basicity and the negatively charged surface which are vital factors for the catalyst-determining reaction mechanism. This work is under review by Applied Catalysis B: Environmental (Yan et al. Applied Catalysis B: Environmental, 2015, under review).

List of abbreviations

BET	Brunauer-Emmett-Teller
CNTs	Carbon Nanotubes
DHA	1,3-dihydroxyacetone
EA	Ethyl Acetate
FTIR	Fourier Transition Infrared Spectroscopy
GLYA	Glyceric Acid
GLYCA	Glycolic Acid
GLYOA	Glyoxylic Acid
GLYHD	Glyceraldehyde
HPYA	Hydroxypyruvic Acid
MOXA	Mesoxalic Acid
OXA	Oxalic Acid
SEM	Scanning Electron Microscope
TARAC	Tartronic Acid
TEM	Transmission Electron Microscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-Rays Diffraction

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Chapter 7 Conclusions and Future Perspectives

7.1 Conclusions

In this study, various approaches for surface functionalization of carbon materials supported catalysts have been explored and employed for selective aerobic oxidation of benzyl alcohol as well as glycerol. Surface-functionalized carbon nanospheres were also utilized as solid base catalysts for aldol condensation reactions. The main discoveries and conclusions of these studies have been summarized in this chapter.

Organosilanes surface functionalized CNTs supported Pd catalysts were synthesized through the facile and rapid post-synthesis grafting and ion adsorption reduction methods for surface functionalization and loading of metallic active phase respectively. These catalysts were successfully applied to the aerobic selective oxidation of benzyl alcohol to benzaldehyde. The catalytic performances are dramatically dependent upon the chemical environment of active sites, physiochemical properties of the functionalized CNTs support surfaces and surface functionalities. The surface oxygen-containing groups improved hydrophilicity and acted as the anchoring sites for either functional groups or metallic nanoparticles. APS functionalized CNTs supported Pd catalyst is superior to either ATMS or HMDS functionalized CNTs supported Pd catalyst for selective oxidation of benzyl alcohol. HMDS contributes to the adsorption barrier caused by the hydrophobic tri-methyl groups attached surface when palladium is adsorbed onto it which results in larger metal particles and lower catalytic activity. Although both APS and ATMS contain amino groups, diamine groups in ATMS have stronger interaction with Pd nanoparticles which hampers exposure of Pd active sites than that of monoamine in APS, hence 1Pd/APS-CNT displays more remarkable enhancement in catalytic activity. The catalytic

performances were in fine tune with the CO stripping measurements where the higher CO electro-oxidation activity correlates the higher catalytic activity for benzyl alcohol oxidation implying the effectiveness of the substantiation from CO stripping characterization. Trace amount of APS covalently σ -bonded onto CNT surface hampers the electron transference between Pd and CNT support, resulting in the difficulties of reaction which is in agreement with the CO stripping voltammetry results. Increasing the APS amount significantly increases the catalytic activity until 1Pd/2.4APS-CNT, the most highly active catalyst in CO electro-oxidation. The abruptly decreased conversion and qTOF of 1Pd/3.6APS-CNT are resulted from the decreased Pd particle exposure due to the excessive amounts of grafted APS groups which possibly form alkanolamine through oligomerization and polymerization on the CNT support.

Considering the complexity of synthesis of organosilanes surface grafted CNTs supported catalysts, nanoparticles-functionalized CNTs supported catalysts were designed for more simplified and effective catalytic process. For investigation of the roles played by rare earth oxides, a series of rare earth oxides functionalized CNTs supported Pd catalysts have been synthesized for selective oxidation of benzyl alcohol. CV background areas are observed decreasing in the sequence of: 1Pd/5La-CNT > 1Pd/5Ce-CNT > 1Pd/5Sm-CNT $\approx$ 1Pd/5Gd-CNT > 1Pd/5Er-CNT > 1Pd/5Yb-CNT > 1Pd/CNT, in correspondence with their surface electron donor properties which can favor the enlargement of areas enclosed by CV curves and this sequence is in agreement with the lanthanide contraction: basicity of rare earth oxides, associated with the electron donor properties declining with the contraction of rare earth cation radius. Samarium oxides exhibited the highest promotion effect for functionalized CNTs supported Pd catalyst in

selective oxidation of benzyl alcohol. However, higher content of Sm surface functionalities hampers the catalytic performance with the optimal content of 5% since high loading of samarium oxides (10%) significantly reduced the relative amount of CNTs, the electro-conductive catalytic support.

Regarding the harsh conditions for CNTs production, a greener and far more inexpensive process of CNS synthesis was introduced by simply the hydrothermal reaction of glucose solution. The as-synthesized CNS was simply functionalized by the alkali treatment approach which can create more abundant hydroxyl and deprotonated –COO⁻ groups. The basic and highly negatively charged surface of CNS can serve as excellent solid base catalyst for aldol condensation reactions with high selectivity toward cinnamaldehyde because the different strength of electric attraction of the positively charged carbonyl groups. Moreover, the resulted more hydrophilic and negatively charged surface of CNS facilitates higher dispersion, smaller size and size distribution of Pd nanoparticles leading to better catalytic performance. 4.2 nm sized Pd particles on CNS-0.5OH presents to be the optimal catalyst due to the contribution from both the coordinatively unsaturated sites and terrace Pd atoms. In addition, strong surface basicity and negative charge contribute to the high selectivity toward benzaldehyde. In the cases of glycerol oxidation, the strong surface basicity favors high catalytic activity for alcohol oxidation. Nevertheless, the selectivity toward DHA obviously decreases in the order of Pd/CNS > Pd/CNS-0.1OH > Pd/CNS-0.3OH > Pd/CNS-0.5OH > Pd/CNS-0.7OH because DHA molecules are instable under conditions of high pH. The oxidation of the secondary OH group in glycerol molecules can be favored under acidic environment, but the stronger acidic environment hampers catalytic activity that glycerol oxidation reaction

may stop at a low enough pH. In contrast, selectivity toward either MOXA or TARAC was increased along with either the enhanced surface basicity or the diminished size of Pd nanoparticles, accompanied by the decreased selectivity toward OXA. Accordingly, by controlling both of the surface amphoteric property and diameters of nanoparticles, the selectivity or yield of specifically targeted valuable product can be controlled.

7.2 Future perspectives

Based upon the discoveries obtained by this PhD work, we proposed some research topics which may be studied in future. According to Chapter 5, it has been proved that rare earth oxides, especially samarium oxides, are very facile and efficient surface functionalities for CNTs supported Pt catalysts. The intrinsic difference and properties of these rare earth elements, such as influence of electron orbits and energy levels on their improvement for catalytic performance are intended to be further explored in detail. Further expansion of rare earth applications are expected accordingly.

Based upon the results reported in Chapter 6, alkali pretreated CNS can be used as solid base catalyst for aldol condensation reaction to synthesize cinnamaldehyde. Thus, utilities of surface-functionalized CNS catalyzing many other high-value base-catalyzed reactions are highly anticipated for investigation. Glycerol is one of the cheapest by-products from diesel industry. The inexpensive process of selective oxidation of glycerol toward high-value chemicals under mild conditions is of great interest of both industries and laboratories. Therefore, the development of highly efficient catalysts for the expected products from glycerol is a crucial job. An organic nitroxyl radical 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) was found to be a selective catalyst for selective oxidation of primary hydroxyl group together with NaOCl as the stoichiometric oxidant,

while selective oxidation of secondary hydroxyl group by anodic oxidation. The effectiveness of this process is comparable to that of biotechnological process in industry. However, TEMPO is expensive and may significant increase the cost of glycerol oxidation process. In the future, inexpensive heterogeneous catalysts are intended to be designed for highly selective glycerol oxidation process. Furthermore, the intrinsic mechanisms of glycerol oxidation toward different products are required to be investigated in detail.

List of abbreviations

CALD	Cinnamaldehyde
CNTs	Multi-Walled Carbon Nanotubes
CV	Cyclic Voltammetry
DHA	1,3-dihydroxyacetone
EA	Ethyl Acetate
EAS	Electrochemical Active Surface
MOXA	Mesoxalic Acid
TARAC	Tartronic Acid
TEM	Transmission Electron Microscopy
TEMPO	2,2,6,6-tetramethylpiperidin-1-oxyl
OXA	Oxalic Acid

Appendix

Journal publications

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