



# **The Development of Pd-based Bimetallic Nano-catalysts in Green Chemistry**

**By**

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## **DECLARATION**

I confirm that this is my own work and the use of all material from other sources has been properly and fully acknowledged.

Fenglin Liao

## **DEDICATION**

To my parents and Zhuoling

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# ABSTRACT

With the gradual depletion of the non-renewable fossil fuel resources and the emerging environmental concerns, the need of exploring renewable synthesis routes of our daily basic stocks is rising. Due to the large contribution to the global primary energy (up to 40% in some countries), biomass has recently been advocated to be one of the most promising alternatives for fossil fuel. This thesis focuses on the catalytic transformations of biomass or biomass derived molecules into valuable small alcohols such as methanol, ethanol, and propanol, which can be used as both fuel and chemical synthesis intermediates.

Novel catalysts with high activity and selectivity toward target products are desperately required in the development of renewable chemical synthesis routes. In the past 200 years, platinum metal catalysts have been widely used in the industry. But nowadays, Pd is attracting increasing attentions due to (i) its similar physicochemical properties to those of Pt, (ii) its higher natural abundance than Pt.

Alloying has been demonstrated as an effective method in enhancing the catalytic properties of noble metals. In this thesis, a new and facile method for the preparation of supported bimetallic NPs with tunable compositions is developed. Through the establishment of a type II hetero-junction in support, controllable amounts of metallic atoms can be derived from the reduction of the metal oxide support, with the assistance of a supported noble metal. A series of extremely small Pd-based bimetallic NPs with a variety of modifier atoms at tunable compositions, namely PdFe, PdCo, PdNi and PdZn, have been synthesized by this method.

These novel bimetallic NPs are applied to the catalytic conversion of biomass or biomass derived molecules containing repeating vicinal diol units. It is demonstrated that the catalytic

performance of Pd in bimetallic phase is governed by the *d*-band structure. The high degree of *d*-band filling and high *d*-band center position favour the selective C-O cleavage in hydrogenolysis of vicinal diol units. On the other hand, the selective C-C cleavage can be achieved by lowering the *d*-band filling of the Pd-based bimetallic NPs. The specificity of C-C bond rupture over that of C-O increases in order of PdZn < PdNi < PdCo < PdFe, with progressive *d*-band filling reduction, eventually reaches 95% in a series of vicinal diols hydrogenolysis. As a result, small alcohols are produced with high selectivity as the degradation products of biomass molecules when PdFe bimetallic NPs are employed as catalyst. Conversely, by incorporating Co atoms at high concentration, PdCo exhibits a high selectivity in breaking C-O bond of ethylene glycol due to the raised *d*-band center position and gives ethanol as the main product. Pd@Zn bimetallic NPs with an imperfect core(Pd)-shell(Zn) structure were used in a methanol synthesis route from biomass transformation via CO<sub>2</sub> hydrogenation (CO<sub>2</sub>/H<sub>2</sub> is produced from low temperature reforming of biomass resource). The Zn shell not only enhances the catalytic activity of Pd metal towards methanol synthesis, but also suppresses the reverse water gas shift (RWGS) reaction in which CO is produced as a by-product. Methanol can be produced as the main product over CO on the Zn rich Pd@Zn surface, even at low pressure. The methanol turnover frequency (TOF) on the exposed Pd site reaches  $1.9 \times 10^{-1} \text{ s}^{-1}$  with a selectivity of 70% at 2 MPa. The enhancement is attributed to the increasing *d*-band filling of Pd@Zn bimetallic NPs by the progressive decoration of Zn on Pd surface, which selectively stabilizes the precursor of methanol (HCOO) over that of CO (COOH). Also, the PdZn catalyst with high ability in dissociating H<sub>2</sub> reduces the activation barrier for methanol synthesis.

The results presented in this thesis, for the first time, signify the possibility of fine-tuning of product specificity of biomass conversion simply by rationally modifying the electronic

properties of the Pd-based catalysts. More importantly, these catalysts will help to diversify the energy generation and relieve our dependence on fossil fuels.

**Keywords:** Pd, hetero-junction, strong metal support interaction (SMSI), biomass, renewable energy, methanol, small alcohol

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## LIST OF SYMBOLS AND ABBREVIATIONS

|              |                                          |
|--------------|------------------------------------------|
| USD          | United states dollar                     |
| K            | rate constant                            |
| A            | Arrhenius factor                         |
| $\Delta E_a$ | activation energy                        |
| R            | ideal gas constant                       |
| PGM          | platinum group metals                    |
| NP           | nanoparticle                             |
| SMSI         | strong metal and support interaction     |
| TEM          | transmission electron microscopy         |
| XRD          | X-ray diffraction                        |
| XPS          | X-ray photoelectron spectroscopy         |
| EXAFS        | extended X-ray absorption fine structure |
| CAL          | cinnamaldehyde                           |
| COL          | cinnamyl alcohol                         |
| MTBE         | Methyl tert-butyl ether                  |
| RWGS         | reverse water gas shift                  |
| TOF          | turnover frequency                       |
| MSR          | methanol steam reforming                 |
| HMF          | hydroxymethylfurfural                    |
| DMF          | dimethylfuran                            |
| PSD          | position sensitive detector              |
| CN           | coordination number                      |
| DW           | Debye Waller                             |
| APR          | aqueous phase reforming                  |

|         |                                                         |
|---------|---------------------------------------------------------|
| WGS     | water gas shift                                         |
| FCC     | face center cubic                                       |
| DFT     | density function theory                                 |
| Pd@Zn   | Pd(core)-Zn(shell) structure                            |
| FWHM    | Full width at half maximum                              |
| CCD     | charge coupled device                                   |
| EELS    | Electron Energy Loss Spectroscopy                       |
| DRS     | Diffusion reflectance spectroscopy                      |
| UV-Vis  | Ultraviolet-visible                                     |
| VB      | valence band                                            |
| CB      | conduction band                                         |
| BG      | band gap                                                |
| PL      | Photoluminescence                                       |
| TRPL    | Time-Resolved Photoluminescence                         |
| TCSPC   | Time-Correlated Single Photon Counting                  |
| FTIR    | Fourier transform infrared                              |
| FFT     | fast Fourier transform                                  |
| EPR     | Electron Paramagnetic Resonance                         |
| NMR     | nuclear magnetic resonance                              |
| TPR     | Temperature programmed reduction                        |
| TCD     | thermal conductivity detector                           |
| ICP-AES | Inductively coupled plasma atomic emission spectroscopy |
| EDA     | ethylenediamine                                         |
| EG      | ethylene glycol                                         |
| 1, 2-PD | 1, 2-propanediol                                        |

|                  |                                     |
|------------------|-------------------------------------|
| 1, 2-BD          | 1, 2-butanediol                     |
| HPLC             | high-pressure liquid chromatography |
| stp              | standard temperature and pressure   |
| GC               | gas chromatography                  |
| PXRD             | Powder X-Ray Diffraction            |
| SXRD             | synchrotron X-ray Diffraction       |
| MAC              | multi-analyzing crystals            |
| GIT              | Gatan imaging filter                |
| $\Delta H$       | Change in enthalpy                  |
| VASP             | Vienna ab initio simulation package |
| PAW              | projector-augmented wave            |
| PBE              | Perdew–Burke–Ernzerhof              |
| GGA              | generalized gradient approximation  |
| SDOS             | surface density of states           |
| EtOH             | ethanol                             |
| PrOH             | propanol                            |
| BuOH             | Butanol                             |
| Temp.            | Temperature                         |
| Conv.            | Conversion                          |
| Select.          | Selectivity                         |
| $Z_{\text{eff}}$ | effective nuclear charge            |
| r.t.             | room temperature                    |
| HOMO             | Highest occupied molecular orbital  |
| LUMO             | Lowest unoccupied molecular orbital |

## LIST OF PUBLICATIONS

1. **F. Liao**, B. Lo, J. Qu, A. Kroner, A. Dent and S. C. E. Tsang\*, *Catal. Sci. Technol.*, **2015**, DOI: 10.1039/C5CY00572H.
2. **F. Liao**, T. Woon B. Lo, S. C. E. Tsang\*, *ChemCatChem*, **2015**, DOI: 10.1002/cctc.201500245R1.
3. **F. Liao**, B. Lo, D. Sexton, J. Qu, C. Ma, R. Chan, Qin Lu, R. Che, W. Kwok, H. He, S. Fairclough, S. C. E. Tsang\* , *ChemCatChem* **2015**, DOI: 10.1002/cctc.201402710.(Front cover paper in ChemcatChem)
4. **F. Liao**, T. Woon B. Lo, D. Sexton, J. Qu, C. Wu, S. C. E. Tsang\*, *Catal. Sci. Technol.* **2015**, 5, 887–896.
5. **F. Liao**, Z. Zeng, C. Eley, Q. Lu, X. Hong\* and S. C. Tsang\*. *Angew. Chem. Int. Ed.* 2012, 124, 5934-5938 (VIP communication paper in Angewandte Chemie)

# Chapter 1 Introduction

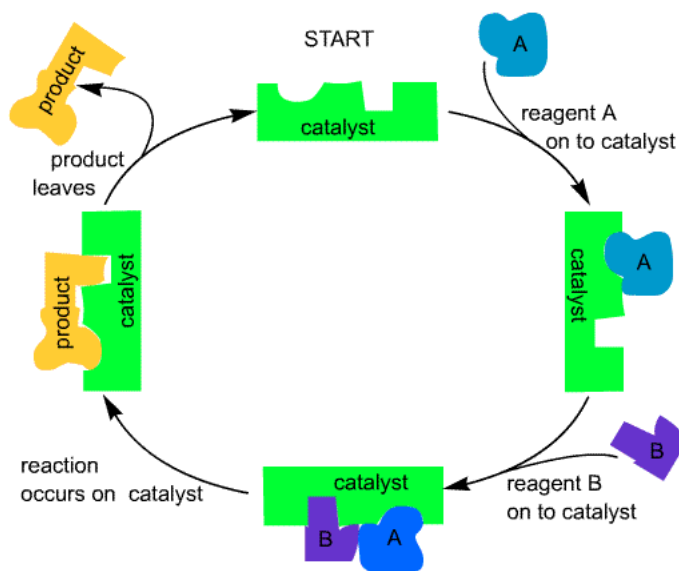
## 1.1 Catalysis

Catalysis is the occurrence of a chemical reaction with accelerated rate due to the participation of an additional substance called a catalyst. The earliest catalysis occurs in nature, the photosynthesis of carbohydrate from carbon dioxide and water in green plants, the alcohol production from fermentation of sugar in the presence of some bacteria, for instance. With the flourishing of human civilization and technology, ‘artificial’ catalysis has been more frequently involved in the industries, including chemical synthesis, energy production, and environmental protection, etc. This reflects the paramount significance of catalysis in our daily life. It is estimated that 90% of all commercially produced chemical products employ catalysts in their manufacturing process. [1] In 2005, catalytic processes generated about \$900 billion in products worldwide. [2] Therefore, catalytic science and technology is regarded as a key factor in development of modern society. [3, 4] The intense investment in catalysis research is increasing year by year owing to the expanding global demand on catalysts at an annual rate of 8% (the demand was estimated at approximately 14 billion USD in 2010). [5]

### 1.1.1 Definition of catalysis

It is part of our daily experience that many chemical reactions, which have a strong tendency to happen from the view point of thermal dynamics, either do not occur, or occur so slowly that their progress is barely observable. For example, a solution of sugar does not degrade to a cup of ethanol; our sea and lakes will not decompose into hydrogen and oxygen even with strong solar irradiation, etc. despite the reactions are thermodynamically favourable. Theoretically, high

temperature is effective for the acceleration of the reaction rates. But in some cases, side reactions become significant at higher temperatures which reduce the yield of desirable product(s). [6] On the other hand, it was found that beer (containing ethanol) can be produced from sugar and water thousands years ago by the addition of a small quantity of yeast at non-extreme conditions at a decent rate. [7] And water can be split into hydrogen and oxygen on the surface of Pt material with natural light. [8] The substances (yeast, Pt, etc.) which by their presence in a system may accelerate these reactions are defined as ‘catalysts’ and these processes as ‘catalysis’ reactions. [6] In a general catalytic process, chemical bonds are broken and new ones are formed repeatedly, without a significant change of the catalyst. While in the absence of the catalyst, this chemical transformation would either not occur or would take place with much lower efficiencies or slower rates. [9] Meanwhile, it is very important to realise that a catalyst cannot initiate a reaction which is thermodynamically unfavourable in an enclosed system. In other words, a catalyst cannot affect the chemical equilibrium of the reaction which is governed by the thermodynamic rule.[6] The description of a typical bond forming catalysis process is illustrated in Scheme 1-1.



**Scheme 1-1** The cycle of catalysis process without catalyst change.

A catalyst usually refers to the matter accelerating the occurrence of target reaction until the chemical equilibrium is reached. A well selected catalyst not only promotes the rate of target reaction, but also shows very low activity in the undesirable ones, which eventually maximizes the selectivity of target product.

### 1.1.2 Principle of catalysis

The principle of catalysis was firstly proposed by the noted Swedish chemist J. J. Berzelius. With the participation of a catalyst, the kinetics of a reaction are affected through the alteration of activation energy of the reaction, without changing the thermodynamics. At the end of the reaction, the catalyst returns to its original form through a series of elementary steps.[10-13] Figure 1-1 shows a schematic diagram which illustrates different energy pathways for a reaction with or without the participation of a catalyst. In addition, catalysts can be atoms, molecules, enzymes, or even solid surfaces.

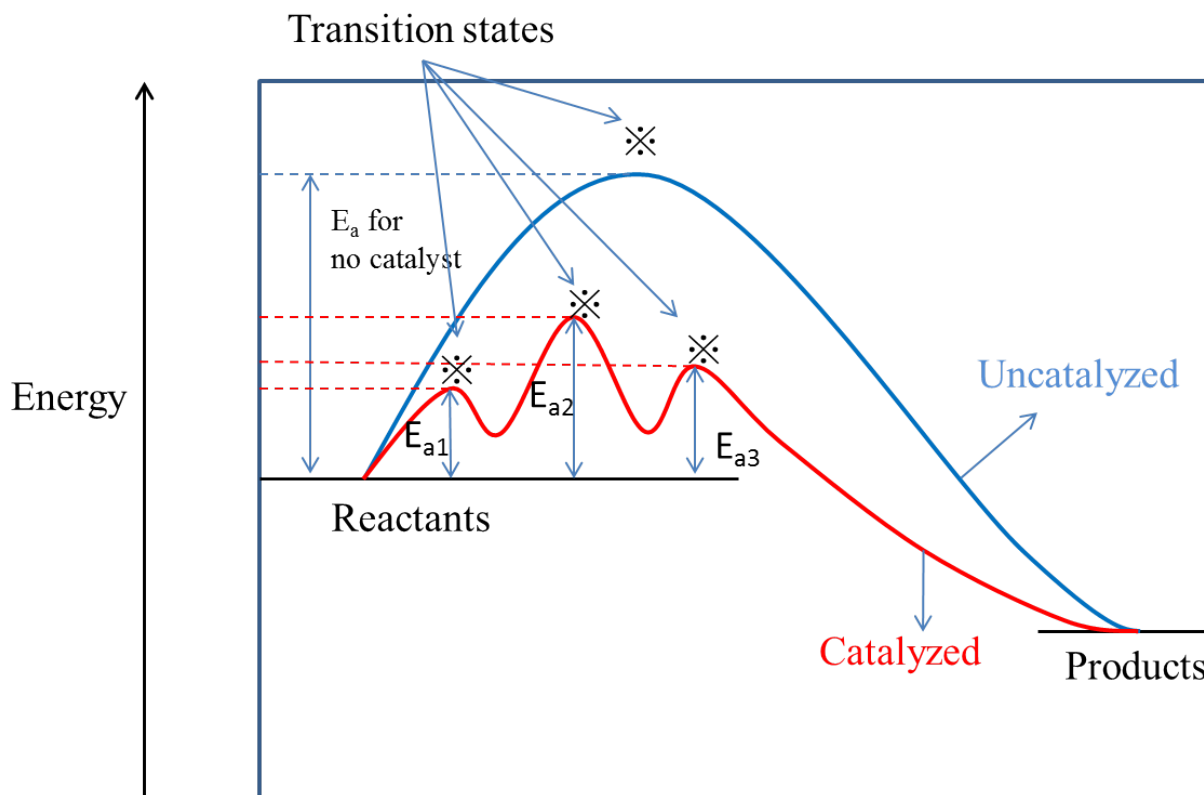


**Figure 1-1** Different energy pathways for a reaction with or without the participation of a catalyst.

As shown in Figure 1-1, the activation barrier of a reaction can be sufficiently reduced by a catalyst. According to the Arrhenius equation:

$$K = Ae^{-\frac{\Delta E_a}{RT}} \quad (\text{Equation 1-1})$$

where  $K$  is the reaction rate constant,  $A$  is the Arrhenius factor,  $\Delta E_a$  is activation energy,  $R$  is the ideal gas constant ( $= 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the reaction temperature. The reaction rate increases exponentially with the decrease of energy barrier. Thereby, the participation of a catalyst can significantly accelerate the rate of reaction.

### 1.1.3 Types of catalysis

Catalysis can be primarily categorized into two types: homogeneous catalysis and heterogeneous catalysis.

Homogeneous catalysis –it is a sequence of reactions that involve a catalyst in the same phase as the reactants. Typically the catalyst(s) and all the reactants are present as a gas mixture or contained in a single liquid phase. A great number of homogeneous catalysts are known, ranging from Lewis and Brønsted acid widely used in organic synthesis, metal ions, metal complexes, organometallic complexes, organic molecules, up to enzymes.[14] In most cases, the active site and the catalysis mechanism of a homogeneous catalyst can be determined and the reaction is quite selective. However, the homogeneous catalyst complexes can be very sensitive to temperature, air, moisture, and are particularly difficult to recycle from the reaction products, which is the major disadvantage. [10] Thus, homogeneous catalysis is often aimed at the production of delicate pharmaceuticals. [15] The market share of homogeneous catalysts is estimated to be only *ca.* 10–15 %. [4]

Heterogeneous catalysis – the catalyst and reactants of heterogeneous catalysis are in different phases and the reactions happen at the interface of the phases. The process involves a sequence of steps:

- (a) The diffusion of gaseous or liquid reactants up to the catalyst surface.
- (b) Association of the reactants with the surface.
- (c) Chemical reaction on the catalyst surface.
- (d) Dissociation of the products from the surface.

(e) Diffusion of the products away from the catalyst. [16]

In a heterogeneous catalytic process, the speed of a chemical reaction is enhanced only at the catalyst surface, which makes the catalytic efficiency much lower than that of homogeneous catalysis. The composition of most catalysts used in heterogeneous catalysis is complicated and the active center is normally vague, which also causes huge difficulties in optimizing the catalytic performance. However, as the reaction occurs at the gas-solid or liquid-solid interface, the reactants, the products and the catalysts can be separated easily, which offers one major advantage comparing with homogeneous catalysis. Therefore, heterogeneous catalysts are the major group of catalysts employed in the bulk chemicals and petrochemicals industry dominating 80% share of the catalyst market. [10, 15] The major advantages/disadvantages of heterogeneous versus homogeneous catalysis are displayed Table 1-1.

**Table 1-1** Comparison of heterogeneous and homogeneous catalysis

| Property          | homogeneous             | heterogeneous  |
|-------------------|-------------------------|----------------|
| catalyst recovery | Difficult and expensive | Easy and cheap |
| Stability         | poor                    | good           |
| Selectivity       | Excellent/good          | Good/poor      |

## 1.2. Pd-based catalysis

Platinum group metals (PGM) constitute the most studied catalyst component for nearly 200 years. [17] In the 19th century, platinum was first used as a catalyst in industrial processes such as the oxidation of sulfur dioxide to sulfuric acid, the oxidation of ethanol to acetic acid or acetaldehyde, and catalytic combustion. [18] Thereafter, the development of new catalysts based

on platinum group metals continues to bloom. The main reasons for the selection of platinum group elements include their intrinsic high catalytic ability under mild conditions, high selectivity towards a specific product, high stability under various reaction conditions and tolerance to poisons, etc. [18] Although platinum is the most widely used PGM element in catalysis, palladium is receiving increasing attention due to its similar catalytic properties to platinum but with wider availability.

Palladium organometallic compounds (homogeneous catalysts) or supported Pd-based nanoparticles (NPs), (heterogeneous catalysts) are both known to be active for a wide range of reactions, which include hydrogenation, oxidation, dehydrogenation, hydrogenolysis, coupling reaction, carbonylation, carbohydrate reforming, hydrodesulphurization.[19-21] Although Pd organometallic catalysts commonly exhibit impressive activity and selectivity with clearly defined catalytic mechanism, the applications in industry remain challenging as they are expensive, generally non-recyclable, and difficult to separate from product mixture. [22-31] Therefore, this thesis focuses on the applications of heterogeneous catalysis by palladium-based catalysts.

The intrinsic catalytic properties of Pd nanoparticles are originated from its fundamental electronic configuration ( $4d^{10}5s^0$ ), which can be strongly influenced by coordination environment.[32] By alloying with a secondary element, anchoring to a support, or controlling particle size, etc., the coordination environment and the electronic band structure of Pd NPs can be controlled and manipulated, which makes it distinctive from that of monometallic Pd. Alloying is one of the mostly investigated methods due to a wide range of choices of the alloying element and well-acquired skills for their syntheses. The alloying method, through inserting a secondary element into the Pd lattice, can affect the coordination environment of Pd by two

aspects: (i) formation of heteroatomic bonds changes the electronic environment of the metal, giving rise to modifications on electronic configuration of Pd through the so called ‘ligand effect’; (ii) the geometry of the bimetallic structure is typically different from its parent metal, e.g., the changes of lattice structure such as metal–metal bond distance and bond angle, which play important roles in fundamental catalysis processes.[33] Therefore, bimetallic nanoparticles consisting of two different elements have been attracting great interest in the fields of science and technology.[34-36] The enhancement of their catalytic performance is assigned to the modified chemical and physical properties of the primary metal by the secondary element.[33, 37] With the expanding demand for efficient catalysts, tremendous experimental efforts have been made in the synthesis of numerous bimetallic catalysts to pursue high activity and selectivity toward the target product. In order to rationally design and produce Pd-based bimetallic catalysts, the modification mechanism of Pd properties by alloying with various elements across the periodic table is receiving increasingly attention. This requires diversified synthesis methods and powerful characterization techniques. (Here the terms ‘alloy’ or ‘bimetallic’ are both used interchangeably without much emphasis whether the added foreign atoms form a true solid solution, islands or core-shell morphology with Pd atoms)

### **1.2.1 Preparation and characterization methods of Pd-based bimetallic NPs**

Since the 1960s, when the importance of bimetallic NPs was started to be recognized, many synthesis methods have been developed, which can be classified into two categories: for unsupported colloidal NPs and for supported bimetallic NPs, respectively. Yonezawa and Toshima have thoroughly reviewed the synthesis methods of preparing unsupported colloidal bimetallic NPs, in which a large amount of organic surfactants are used as stabilizers.[38] Consequently, the surface of these bimetallic NPs is mainly covered by a layer of surfactant

molecules which reduce the number of exposed metal site for catalysis. Also, the small colloidal NPs without support are more prone to aggregate under reaction conditions after the total removal or partial removal of the surfactant. Therefore colloidal metallic NPs are mainly used as model materials to investigate the alloy properties comparing with their monometallic NPs. [38] In contrast, supported alloy or bimetallic NPs as catalysts are practically more useful for a wider range of industrial reactions. Thus, we mainly focus on the preparation of the supported Pd-based alloy NPs.

#### **1.2.1.1 Co-impregnation**

Co-impregnation is one of the most compatible methods for the preparation of supported bimetallic or alloy Pd based NPs.[32] Briefly, an inert support is immersed into a solution mixture composed of palladium and the secondary element precursors with a volume equaling to the total pore volume of the support material. Accompanying the evaporation of solvent, the complex precursors of Pd and other element are simultaneously deposited on the surface of support. After thermal reduction at elevated temperature, Pd-based NPs can be synthesized accordingly. The preparation of PdCu bimetallic NPs by the co-impregnation method was successfully achieved by Haller and his co-workers. [39]  $\text{Pd}(\text{NO}_3)_2$  and  $\text{Cu}(\text{NO}_3)_2$  were used as the precursors with variable mole ratios to control the ratio of Pd: Cu in their resulting alloy NPs. This method is convenient and simple, but the precursors in solution generally have poor interaction with each other, hence the formation of bimetallic species is not expected to take place in the impregnation or deposition step. Instead, the formation of bimetallic NPs precursor is thought to happen on the surface of the support during the subsequent thermal or reduction steps.[40] Thus, the composition of the bimetallic NPs on the support surface could be unevenly distributed if the latter processes are improperly carried out. For example, too rapid thermal

heating or reduction of deposited precursors on the support surface may result in phase segregation. Also, compared to other methods described later in this thesis, the particle size prepared by this method is relatively large due to the required high temperature for thermal reduction.

#### **1.2.1.2 Sequential impregnation**

In the co-impregnation method, the two elemental precursors of bimetallic NPs are deposited on the surface of the support simultaneously, while in the process of sequential impregnation the two elements are introduced sequentially, as the name suggests. The procedure involves several steps: a metallic complex containing one element (the Pd or the modifier element) is first deposited on an inert support. Then, a subsequent thermal treatment at elevated temperature is required to partially remove the ligands of the central metal atom. Thereafter, the secondary-element-containing complex is introduced to react with this unsaturated species with the formation of supported bimetallic species. Following pre-reduction in a hydrogen atmosphere, the bimetallic NPs can be produced. The synthesis of Pd-based alloys using this method is widely reported in literature: PdPt by Auvray, [41] PdRh by Araya, [42] PdCu by Yaakob, [43] etc. The composition of the alloy NPs prepared by this approach can be very uniform if the synthetic procedure is carefully controlled, also the concentration of the produced bimetallic sites is generally higher than that produced by the conventional co-impregnation method. [40] However, the whole procedure involves many steps and usually requires exquisite thermal treatments, which may be difficult to handle at industrial scale. [40]

### 1.2.1.3 Thermal decomposition of molecular bimetallic cluster

The thermal decomposition of molecular bimetallic clusters is another promising method for the preparation of highly dispersed supported Pd-based alloy or bimetallic catalysts. The rapid developments in the synthesis of organometallic complexes provide a wide range of heteroatomic metal clusters of palladium incorporated with other elements of tunable sizes. [44] This synthetic method involves adsorption of a bimetallic cluster precursor on a support, followed by a thermal treatment in an inert atmosphere or hydrogen to remove the ligands from the cluster frame. Braunstein *et al.* reported that extremely small PdFe clusters can be prepared by the decomposition of  $[\text{FePd}_2(\text{CO})_4(\text{dppm})_2]$  or  $[\text{Fe}_2\text{Pd}_2(\text{CO})_5(\text{NO})_2(\text{dppm})_2]$  on a  $\text{SiO}_2$  support.[45] Typical transmission electron microscopy (TEM) images show the average particle size can be as small as 1-2 nm. The metallic NPs are normally well dispersed and the composition is uniform. The key factor of success relies on a strong bonding between Pd and the other element in their molecular cluster. If the interaction is not strong enough compared to the affinity for the individual metal with the support surface, the heteroatomic cluster framework is prone to segregate upon adsorption, resulting in the formation of two separated types of monometallic NPs on surface. Thus, this preparation method typically requires a precise synthesis of a stable organobimetallic complex. The main drawbacks of this method are the high cost for the organobimetallic complex synthesis and the thermal instability of the produced bimetallic NPs on the support surface. After the formation of bimetallic NPs on the support (typically  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$ ), the weak interaction between support and NPs does not offer much attenuation to the extent of their aggregation or sintering on the surface.

#### 1.2.1.4 Co-reduction of PdO/support oxide

Metal nanoparticles supported on high surface area oxides are the most widely used catalysts in industrial reactions.[46] It has been demonstrated that many catalytic reactions require a specific strong metal and support interaction (SMSI) to give a high catalytic performance.[47] The underlying principle for the modification of metal nanoparticles by the support material is not well understood. It is becoming clear that one of the important causes for SMSI is the decoration of supported metal particles with reactive metallic elements derived from the deep reduction of the support. This is especially pronounced in supported noble metal systems with the NPs capable of activating and transporting hydrogen for the deep reduction of the support. Taking the traditional Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst for methanol production from synthesis gas as an example, recent research using advanced and sensitive instruments has shown that a very small quantity of Zn atoms is reduced from ZnO at the interface of Cu/ZnO by atomic H produced from the Cu site. This generates catalytically active CuZn sites, which are believed to exhibit distinctive electronic properties from monometallic Cu, and gives enhanced catalytic performance. [48, 49] Similarly, He and Chin *et al.* reported that PdZn can be formed during the hydrogen pre-treatment of PdO/ZnO. Pd is more active than Cu in dihydrogen activation to form active H atoms, which promotes more extensive reduction of ZnO.[50, 51] Oyola-Rivera *et al.* reported the *in situ* formation of Pd<sub>2</sub>Ga phase from Pd/Ga<sub>2</sub>O<sub>3</sub> during the CO<sub>2</sub> hydrogenation to methanol and dimethyl ether.[52] From these results, it is clear that co-reduction of PdO/support oxide can be used as a synthetic tool for the preparation of Pd-based bimetallic or alloy NPs. Owing to the strong interaction with the support, the supported Pd containing NPs prepared by this method are well dispersed and also exhibit high stability in the catalytic reaction. However, the as-synthesized metallic NP is usually Pd rich due to the reduction tolerance of support oxide at mild

conditions which leads to a limited production of the modifier atom from the support reduction. It is noted that mild reduction conditions are required to maintain the small particle size of the metallic NPs whilst high temperature treatment would cause sintering of NPs. Consequently, the ratio of Pd: modifier in the bimetallic phase is uncontrollable. In addition, the alloying process usually occurs at the interfaces of Pd and the support. Due to the complexity and diversity of the interfaces, the composition of produced bimetallic NPs is usually uneven. Also, from the viewpoint of theory, it is difficult to assign the observable superior properties of the catalyst to bimetallic effect exclusively owing to the tangling of SMSI.

#### **1.2.1.5 The characterization of bimetallic NPs**

The common characterization techniques for bimetallic NPs include transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), extended X-ray absorption fine structure (EXAFS). XRD is one of the most widely used characterization techniques for a wide range of materials and it provides information of lattice structure, crystallite size, particle composition, atom arrangement, etc. Based on Vegard's law, XRD can be used to estimate the composition of bimetallic NPs, as the diffraction peak position and the lattice parameter vary smoothly as a function of the composition. However, this technique can only be applied to particles with long range periodic atomic arrangement; when the particle size is smaller than 3 nm, no clear diffraction peak can be observed. TEM is a powerful tool to visualize the bimetallic NPs directly (revealing the morphology, dispersion, lattice spacing, etc.). By Fourier transformation, an indexed electron diffraction pattern of a nano-area can also be obtained which may reflect the lattice structure of the individual bimetallic NPs, if the selection of indexed area is appropriate without a strong influence of the support. XPS is often used in the analysis of chemical compositions of bimetallic NPs by taking their sensitivity factors into

account.[53] Also, the recorded variation of binding energies is related to the electronic environment of an element in the bimetallic phase reflecting the electronic interaction of Pd with the modifier atoms. Distinguished from the techniques mentioned, EXAFS provides the local structure information of the material. It usually reveals the micro-chemical environment of an absorbing element, which helps to identify the bond interaction of Pd with the other element in bimetallic NPs at atomic scale, excluding the disturbing of bulk support. The detailed principles and the applications of these characterization tools will be thoroughly reviewed in Chapter 2. Usually, a series of techniques are combined to provide the accurate information on the structure and composition(s) of the supported Pd bimetallic NPs.

### **1.2.2 Applications of Pd-based bimetallic NPs in ‘green’ catalysis**

As stated, Pd-based catalysts show a wide range of applications in catalysis. With the modification of the secondary element, supported Pd bimetallic NPs are capable of catalyzing many reactions, e.g. hydrogenation, dehydrogenation, hydrogenolysis, carbohydrates reforming, oxygen reduction reaction, with superior ability to many other metals. Meanwhile, with the rapid development of economy and human population, the conflict of expanding energy demand with the exhaustion of fossil fuel reserves and aggravation of environment is getting increasingly intense. Therefore, the precious metals, such as Pt, Pd, Rh, etc., with excellent catalytic ability are more favoured to be applied in ‘green’ catalysis processes. These help to develop new renewable chemical synthesis routes, to increase energy utilization efficiency, to improve the environment issues, etc. Some recent advances of Pd-based catalysis in ‘green’ chemistry are briefly reviewed in this section.

### 1.2.2.1 Hydrogenation of CO<sub>2</sub>

Catalytic hydrogenation of unsaturated bonds is an important chemical step in the chemical industry. Pd-based catalysts are highly active in this type of reactions due to the superiority of Pd in dissociating the H<sub>2</sub> molecule into atomic H, which is attributed to the appropriate strength of Pd-H bond. The ‘volcano’ relationship of H<sub>2</sub> activation ability with M-H (M=metal) bond energy is clearly shown in Figure 1-2. The Pd metal locates in the top area of ‘volcano’ plot, which implies its excellent capability in catalyzing hydrogenation reactions. [54] With the modification of a secondary element, Pd-based bimetallic NPs are widely employed in a series of industrial hydrogenation processes, e.g. the total hydrogenation of benzene to cyclohexane, partial hydrogenation of alkynes to alkenes, selective hydrogenation of cinnamaldehyde (CAL) to cinnamyl alcohol (COL), etc. Also the catalytic performance of Pd can be optimized by the appropriate choice of modifier elements.

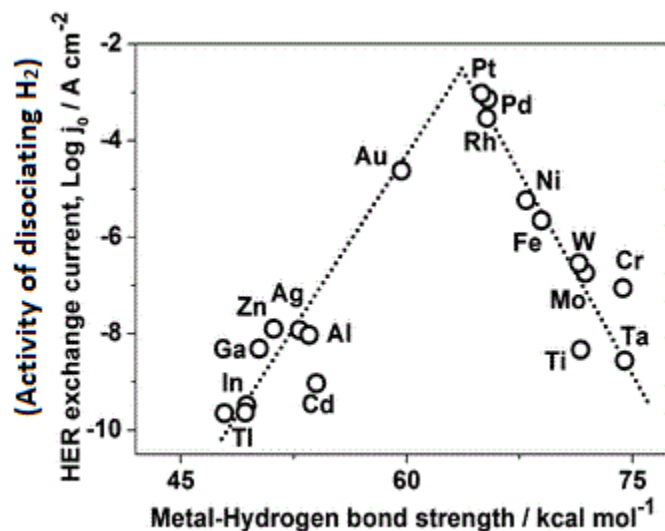


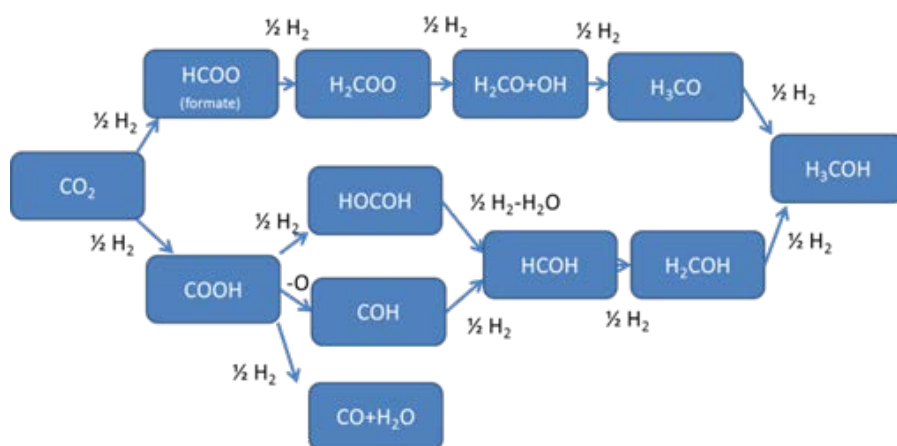
**Figure 1-2** The volcano relationship of the metal-hydrogen bond strength and the activity of dissociating  $H_2$  (the activity is represented by the exchange current value in  $H_2$  evolution reaction (HER) with various metal as the electrode, the figure is from reference 54)

Due to the rapid consumption of fossil fuel required by the blooming of economy since 19th century, concentration of  $CO_2$  in atmosphere is increasing year by year which is causing the climate change because of the position of  $CO_2$  as the primary greenhouse gas.[55,56] Recently, intense investment has been devoted into the capture of  $CO_2$  by various ways. With the developments of techniques for large scale production of  $H_2$  from renewable source (solar energy, hydropower, biomass, excess chemical heat, etc.), [57, 58] the hydrogenations of  $CO_2$  to value-added chemicals have become a hot issue in catalysis chemistry. [59, 60]

In particular, the hydrogenation of  $CO_2$  to methanol looks very attractive due to the position of methanol as a high energy density liquid fuel and a key chemical intermediate (for manufacture of formaldehyde, methyl tert-butyl ether (MTBE), acetic acid, etc.).[61] The traditional catalyst for methanol synthesis is  $Cu/ZnO$ . [62,63] It is reported by Haller and Fierro *et al.* that a small

amount of Pd addition into the Cu/ZnO catalyst can enhance the methanol production activity due to the synergy effect between Pd and Cu atoms through the formation of PdCu alloy.[64,65] The enhanced activity of the alloy is thought to be caused by the hydrogen spillover from Pd to Cu, which accelerates the hydrogenation rate of adsorbed carbonaceous species to methanol on the Cu site. Pd-based catalyst is supposed to give higher activity in CO<sub>2</sub> hydrogenation than the Cu-based ones due to the known superiority of Pd in activating hydrogen molecules. However, the monometallic Pd dispersed on inert support (Pd/TiO<sub>2</sub>, Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/SiO<sub>2</sub>) shows very low activity and selectivity towards methanol synthesis. This is caused by the weak adsorption of CO<sub>2</sub> on pure Pd surface and the existence of reverse water gas shift (RWGS) reaction producing CO as the by-product. (The proposed pathways in CO<sub>2</sub> hydrogenation are shown in Scheme 1-2; [66] methanol synthesis and CO production are in parallel to each other). Bonivardi *et al.* reported the Pd/SiO<sub>2</sub> catalyst with incorporation of Ga<sub>2</sub>O<sub>3</sub> showed a 500 fold Pd turnover frequency (TOF) of monometallic Pd/SiO<sub>2</sub> and the enhancement is ascribed to the formation of Ga-Pd interaction. The alloy surface is thought to strengthen the stability of methanol synthesis intermediates, including formate and methoxy species. [67] Iwasa *et al.* investigated a series of Pd alloys including PdZn, PdIn and PdGa etc., which are formed *in situ* from the reduction of Pd/metal oxides (ZnO, In<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>, etc.) and they exhibit methanol production activities in the order of PdZn > PdIn > PdGa at 1 atmosphere (Table 1-2, as indicated by the rate of methanol formation and TOF value for methanol synthesis).[68] By combining the experimental results and the theoretical calculations, it was reported that there is an electron charge transfer from the late transition metal (Ga, In, Zn) to Pd, which modifies the density of states of the valence band for the alloys to resemble Cu. This stabilizes the methanol synthesis intermediates such as formate and methoxy. [66, 69, 70] The relationship of formate stability on metal surface and the

formation heat of metal formate salt is shown in Figure 1-3. It is noted that the heat formation of copper formate is much higher than that of palladium formate indicating the higher ability of Cu in stabilizing formate species in the CO<sub>2</sub> hydrogenation reaction. Due to the higher ability in activating hydrogen molecules, Pd-based alloys show 20-100 times higher activity (in terms of TOF) than Cu, which makes them more promising in CO<sub>2</sub> hydrogenation.



**Scheme 1-2** The proposed pathways in CO<sub>2</sub> hydrogenation to methanol and RWGS.

**Table 1-2** The catalytic performances of Pd-based catalysts in CO<sub>2</sub> hydrogenation at 1 atmosphere at 463 K, CO<sub>2</sub>:H<sub>2</sub> = 1:9 (from reference 68).

| Catalyst                              | Rate of formation<br>( $\mu\text{mol min}^{-1} \text{g}^{-1}$ ) |       |                 | Methanol<br>selectivity<br>(%) | Methanol<br>TOF $\times 10^3$<br>(s <sup>-1</sup> ) |
|---------------------------------------|-----------------------------------------------------------------|-------|-----------------|--------------------------------|-----------------------------------------------------|
|                                       | CH <sub>3</sub> OH                                              | CO    | CH <sub>4</sub> |                                |                                                     |
| <b>Pd/ZnO</b>                         | 1.28                                                            | 0.682 | 0.01            | 65.1                           | 1.1                                                 |
| <b>Pd/Ga<sub>2</sub>O<sub>3</sub></b> | 0.169                                                           | 0.607 | 0.01            | 23.3                           | 0.12                                                |
| <b>Pd/In<sub>2</sub>O<sub>3</sub></b> | 0.246                                                           | 15.4  | 0.01            | 1.72                           | 0.21                                                |
| <b>Pd/SiO<sub>2</sub></b>             | 0                                                               | 0.522 | 0.09            | 0                              | 0                                                   |
| <b>Pd/ZrO<sub>2</sub></b>             | 0.222                                                           | 13.2  | 0.54            | 1.65                           | 0.06                                                |
| <b>Pd/Black</b>                       | 0                                                               | 0.431 | 0.02            | 0                              | 0                                                   |
| <b>Cu/ZnO</b>                         | 1.74                                                            | 3.96  | 0               | 30.4                           | 0.075                                               |

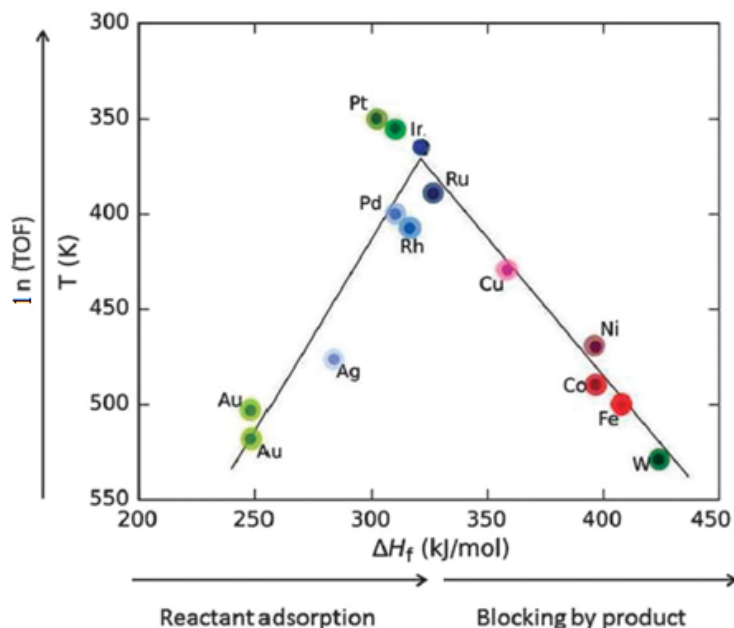


**Figure 1-3** ‘Volcano’ plot: a plot of decomposition temperature of transition metal formate at normalized rate (an alternative axis on natural logarithm of turnover frequency,  $\ln(\text{TOF})$  at the corresponding temperature) as a function of heat of formation ( $\Delta H_f$ ) of transition metal formate (from reference 71).

The detailed mechanism of incorporating modifier atom to Pd to alter its properties is still unclear. From electronic configurations, all the late transition metals including (Zn, In, Ga) with s-valence electrons can transfer their charge (electrons) to Pd due to the empty Pd 5s-orbital. This increases the electron density of the Pd-based alloy surface, which enhances the interaction(s) with intermediates in a high oxidation state and catalyzes further reduction of  $\text{CO}_2$ .

#### 1.2.2.2 *In-situ* hydrogen production for fuel cell

A fuel cell is a device that converts the chemical energy from a fuel into electricity through a chemical reaction with dioxygen or another oxidizing agent. Compared with the traditional internal combustion engine, fuel cells show several major advantages: [72]

- (i) The energy efficiency of fuel cell is higher.
- (ii) Most fuel cells are operated more silently which reduces noise pollution.
- (iii) Fuel cells produce less pollution products.

Thereby, concerning the aggravating problems of energy and environment, the development of fuel cells is receiving growing attention to increase energy efficiency and reduce environment pollution. Until now, fuel cells operate best on pure  $H_2$  with high energy efficiency and no pollution, as hydrogen is the simplest resource molecule which simplifies the reaction process significantly. [72, 73] But as the lightest gas - difficult to be liquefied, its high pressure storage and transportation are considered to be inefficient, particularly in the use of fuel cell. An instant  $H_2$  production from steam reforming reactions of liquid hydrocarbons could be a feasible solution. [74]

Formic acid is regarded as a convenient  $H_2$  storage chemical for supplying  $H_2$  to fuel cells due to its high energy content and low decomposition temperature.[75-77] It has been widely reported that formic acid can be dehydrogenated under 100 °C catalyzed by Pd.[77-80] However, accompanying the dehydrogenation process,  $HCOOH$  can also be dehydrated to produce  $CO$  and  $H_2O$  as the products.[80] For the subsequent conversion of hydrogen into electrical energy, the latter pathway that produces  $CO$  as an impurity, which is toxic to fuel cell catalysts, should be avoided.[77] Gu *et al.* reported that a supported monometallic Pd catalyst shows high activity in decomposing formic acid initially but deactivates quickly due to  $CO$  poisoning.[81] After a screening of a large variety of mono- or bimetallic catalysts, supported AuPd alloy is found to exhibit the highest activity with an excellent stability for the dehydrogenation of  $HCOOH$  to  $H_2$ . It is also proved that the enhancement should be attributed to the high  $CO$  tolerance of the alloy by the incorporation of Au. With the same principle, Sen Zheng *et al.* prepared a PdAg alloy

with controllable composition successfully and they showed that Pd<sub>58</sub>Ag<sub>42</sub> NPs is the best catalyst for the reaction. An initial TOF of 382 h<sup>-1</sup> with an apparent activation energy of 22 kJ mol<sup>-1</sup> were obtained.[82] Barteau and Hoshi *et al.* proposed that the CO<sub>2</sub> and CO are generated from the decomposition of formate species in distinguished adsorption states, as shown in Figure 1-4 a, b: the adsorbed bidentate form leads to the production of CO<sub>2</sub> while the adsorbed monodentate form is the precursor of CO.[83, 84] The enhancement of electronic back donation from the Pd-based surface to the formate species could strengthen the adsorption of bidentate and favours the dehydrogenation pathway. To tune the interaction of Pd with the adsorbed formate species, a series of core-shell Pd(shell)M(core) alloys were prepared by Tedsree *et al.* A negative linear correlation between catalytic activity of HCOOH dehydrogenation and the work function of the metal core was observed (Figure 1-4(c)).[85] This work clearly indicates that the enhancement of catalytic performance is caused by the electron transfer from the core metal to the Pd shell, which increases the electronic donation from Pd surface to the adsorbed formate and enhance the adsorption strength of the bidentate form. As a result, Pd(shell)Ag(core) alloy is found to display the highest selectivity of CO<sub>2</sub> due to the lowest work function of Ag.

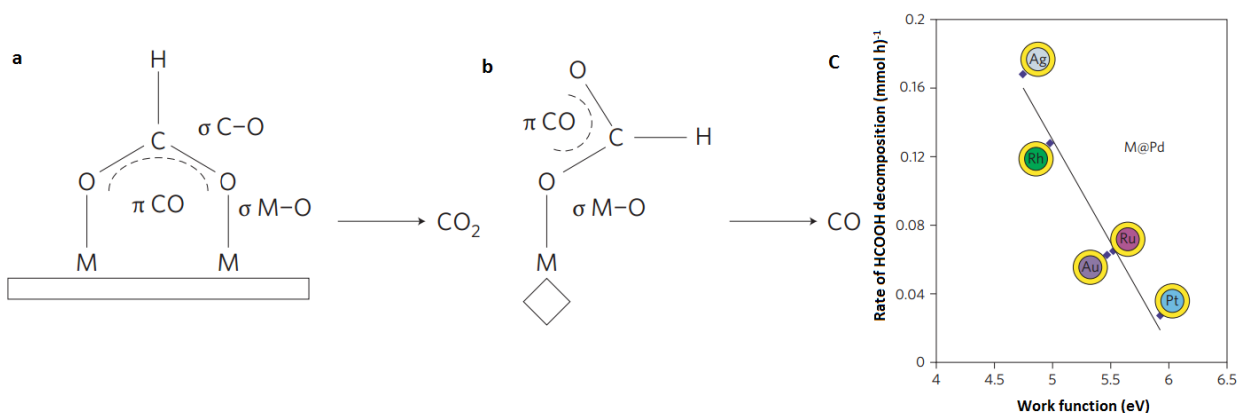


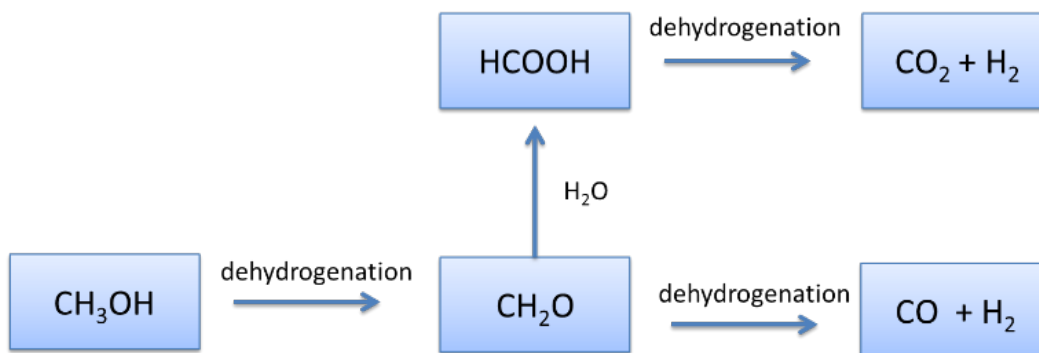
**Figure 1-4** Summary of the interactions of (a) bridging formate (bidentate) on a flat terrace of metal M sites and (b) linear formate (monodentate) on isolated or low coordinated M sites (from reference 83 and 84). (c) Correlation between the M core work function and the rate of dehydrogenation of HCOOH with M@Pd as the catalysts (from reference 85).

Another frequently employed carbohydrate for *in situ*  $\text{H}_2$  production in the use of fuel cell is methanol due to its high ratio of H:C (4:1), its industrial availability, relatively low reforming temperature and low sulfur content.[50,86-89] Previous studies of methanol steam reforming (MSR) to  $\text{CO}_2$  and  $\text{H}_2$  were focused on the use of Cu-based catalysts.[90-92] However, the Cu-based catalysts show poor thermal stability and are pyrophoric, which are not suitable for general fuel cell applications.[51] Recently, investigation is shifting towards Pd-based catalysts. As Iwasa *et al.* reported, monometallic Pd shows very low activity and selectivity for the MSR reaction due to the decomposition of methanol to CO, which not only reduces the  $\text{H}_2$  yield but also causes the deactivation of the catalyst (through CO poisoning). [93] But Pd/ZnO is found to be an excellent catalyst for the MSR reaction due to the modification of Pd by reactive Zn atoms from the reduction of underneath ZnO support.[51,94] PdZn is then regarded as the active phase. In addition, it is reported that  $\text{CO}_2$  selectivity of the MSR reaction is related to the ratio of Pd: Zn

in the alloy. The PdZn alloy with relatively higher Zn content show higher activity and higher CO<sub>2</sub> selectivity.[95-97] Zhang *et al.* recently reported PdZn  $\beta$ -phase (Pd:Zn =1:1) was prone to form on polar (0001) facets of ZnO rather than on nonpolar (10-10) facets.[50] Thus, the catalytic ability can be further enhanced by the morphology control of the support. A series of Pd-based catalysts are synthesized and screened by Iwasa *et al.* Besides Pd/ZnO, PdGa and PdIn formed during *in situ* reduction of Pd/metal oxide (Ga<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>) are also reported to show enhanced performances with an excellent CO<sub>2</sub> selectivity comparing to monometallic Pd, as illustrated in Table 1-3. The activities of the catalysts in term of H<sub>2</sub> TOF order as Pd/ZnO>Pd/In<sub>2</sub>O<sub>3</sub>>Pd/Ga<sub>2</sub>O<sub>3</sub>.[98] The possible reaction pathways of the MSR reaction are shown in Scheme 1-3. Takezawa *et al.* proposed that the role of the additive atoms is to stabilize the adsorbed formaldehyde and to facilitate the attack of H<sub>2</sub>O to produce formic acid which further decomposes to CO<sub>2</sub> and H<sub>2</sub>.[98]

**Table 1-3** The catalytic performance of a series of Pd-based catalyst in the MSR (reaction temperature = 493 K, inlet partial pressure of methanol = 10.1 kPa, Pd loading = 10 wt%) (from reference 98).

| catalyst                              | conversion | selectivity     |      |      | H <sub>2</sub> TOF |
|---------------------------------------|------------|-----------------|------|------|--------------------|
|                                       |            | CO <sub>2</sub> | CO   | DME  |                    |
| <b>Pd/ZnO</b>                         | 54.2       | 99.2            | 0.8  | 0    | 0.497              |
| <b>Pd/In<sub>2</sub>O<sub>3</sub></b> | 28.3       | 95.5            | 4.5  | 0    | 0.291              |
| <b>Pd/Ga<sub>2</sub>O<sub>3</sub></b> | 21.2       | 94.6            | 5.4  | 0    | 0.177              |
| <b>Pd/SiO<sub>2</sub></b>             | 15.7       | 0               | 100  | 0    | 0.021              |
| <b>Pd/Al<sub>2</sub>O<sub>3</sub></b> | 58.9       | 0               | 69.6 | 30.4 | 0.036              |
| <b>Pd/MgO</b>                         | 41.0       | 6.6             | 93.4 | 0    | 0.053              |
| <b>Pd/ZrO<sub>2</sub></b>             | 64.3       | 18.4            | 81.6 | 0    | 0.139              |
| <b>Pd/CeO<sub>2</sub></b>             | 62.4       | 22.7            | 77.3 | 0    | 0.025              |
| <b>Pd/Ta<sub>2</sub>O<sub>3</sub></b> | 6.0        | 0               | 100  | 0    | N.A.               |
| <b>Pd/HfO<sub>2</sub></b>             | 13.6       | 0               | 100  | 0    | N.A                |
| <b>Pd/black</b>                       | 10.9       | 0               | 100  | 0    | 0.0071             |
| <b>Cu/ZnO</b>                         | 19.3       | 100             | 0    | 0    | 0.300              |

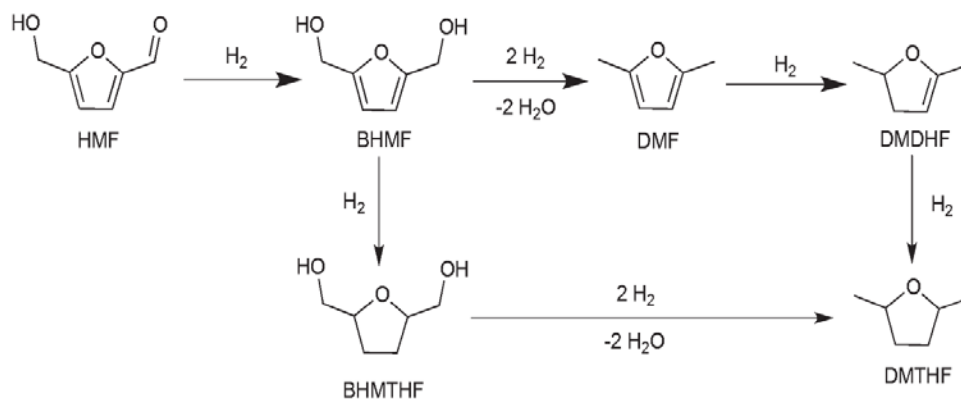


**Scheme 1-3** The parallel pathways of CO and CO<sub>2</sub> production in the MSR reaction.

### 1.2.2.3 Conversion of biomass to value-added chemicals

It is well accepted that our present non-renewable natural resources (oil, gas, coal) cannot dominate the energy and chemical markets for too long time due to their finite reserve and rapid consumption.[99-102] As one of the primary renewable energy resources in nature, biomass especially the carbohydrates with repeating  $-\text{CH}(\text{OH})\text{CH}(\text{OH})-$  units becomes a favourable alternative.[103] Hydrogenolysis is widely used as a first step of the utilization of biomass molecules to produce value-added chemicals. The catalytic process usually involves the cleavage of C-C or C-O bonds of  $-\text{CH}(\text{OH})\text{CH}(\text{OH})-$  units by the produced atomic hydrogen on a catalyst surface. Monometallic Pd catalyst is found to be highly active in C-O hydrogenolysis. Mitra *et al.* reported the hydrogenolysis of 5-hydroxymethylfurfural (HMF, a glucose derivative) catalyzed by Pd/C. 2,5-dimethylfuran (DMF) that produced from the hydrogenolysis of C-O bond and its further hydrogenation products are observed to be the main products.[104] The reaction pathways are displayed in Scheme 1-4. Huber reported the application of a Pd catalyst in the production of renewable alkane from the C-O bonds hydrogenolysis of biomass molecule with sorbitol as the substrate. The alkane selectivity reaches 98% implying complete elimination of the C-O bond. [105] However, due to the high reaction temperature employed, some of the C-C bonds in  $-\text{CH}(\text{OH})\text{CH}(\text{OH})-$  units are also cleaved which increases the selectivity towards lighter alkanes at the expense of higher alkanes. Wu *et al.* (our group) first reported methanol synthesis from the selective C-C hydrogenolysis of ethylene glycol (the simplest biomass derived molecule) over Pd/Fe<sub>2</sub>O<sub>3</sub>, which opened up a new renewable non-syngas route for methanol production.[106] The *in situ* formed PdFe alloy nanoparticles supported on Fe<sub>2</sub>O<sub>3</sub> are believed to provide active sites for the hydrogenolysis reaction. The coordination of Fe atoms around each Pd atom shown by EXAFS (Table 1-4, as indicated by the existence of Pd-Fe scattering path)

confirms the formation of PdFe. Unfortunately, due to the insufficient production of Fe modifier atoms from the *in situ* reduction of Fe<sub>2</sub>O<sub>3</sub>, some Pd clusters are also present (as shown in Table 1-4, the Pd-Pd scattering path in Pd fcc structure is also observed) and the products distribution of the hydrogenolysis is broadened.



**Scheme 1-4** Hydrogenolysis of HMF under H<sub>2</sub> (30 psi) with Pd/C as the catalyst (from reference 104).

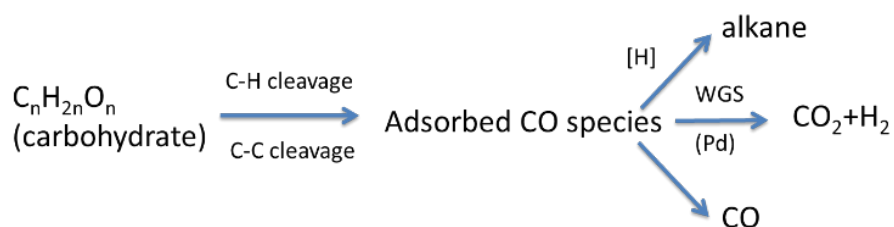
**Table 1-4** The EXAFS result of the Pd/Fe<sub>2</sub>O<sub>3</sub> catalyst for the hydrogenolysis of ethylene glycol (from reference 106).

| Sample                                                                           | Scattering pair    | CN     | R-factor | $\Delta E$ (eV) | DW factor ( $\sigma^2 \times \text{\AA}^2$ ) |
|----------------------------------------------------------------------------------|--------------------|--------|----------|-----------------|----------------------------------------------|
| <b>Pd/C</b><br><br><b>Pd/Fe<sub>2</sub>O<sub>3</sub></b><br><b>(pre-reduced)</b> | Pd-Pd <sup>b</sup> | 8.0(3) | 2.6%     | -7.6            | 0.006                                        |
|                                                                                  | Pd-Fe <sup>a</sup> | 1.0(2) |          |                 | 0.003                                        |
|                                                                                  | Pd-Pd <sup>a</sup> | 1.9(2) | 1.6%     | -7.4            | 0.004                                        |
|                                                                                  | Pd-Pd <sup>b</sup> | 2.4(2) |          |                 | 0.003                                        |

(CN, coordination number; DW, Debye Waller;  $\Delta E$ , the absorbing energy difference between the experiment value and the calculated value in the fitting; R-factor is the indication of fitting quantity; all these factors are in a reasonable range of EXAFS fitting; <sup>a</sup>, <sup>b</sup> indicate the scattering paths derived from PdFe(1:1) face center cubic structure (fcc) and Pd fcc structure, respectively)

Besides hydrogenolysis, aqueous phase reforming (APR) is another widely used method for biomass utilization producing hydrogen. Hydrogen gas is considered as the cleanest energy carrier. However, its large scale production is presently derived from steam reforming of natural gas, which is obviously unsustainable. Thus, hydrogen production from the aqueous phase reforming (APR) reaction of biomass molecules is receiving increasing attentions and being regarded as an alternative route to obtain renewable hydrogen.[107-109] The desired reaction pathways involve cleavage of C–C bonds as well as C–H and O–H bonds to form adsorbed CO species on the catalyst surface which is then removed by the water-gas shift reaction (WGS) to form CO<sub>2</sub> and H<sub>2</sub> (as shown in Scheme 1-5).[110] However, the hydrogenation of the adsorbed CO species by the *in situ* formed H<sub>2</sub> may also produce alkanes as by-products, which reduces the overall H<sub>2</sub> yield. Pt metal is found to be the most active monometallic catalyst for the APR followed by Ni > Ru > Rh ≈ Pd > Ir, but Pd is known to be the most selective metal in H<sub>2</sub> production. [109] Thus, the modification of Pd to enhance the activity is being intensively investigated due to the relatively lower cost of Pd than Pt and the demand for higher H<sub>2</sub> selectivity over alkanes. Huber *et al.* reported that metallic iron atoms have an extremely strong promotional effect on the activity of Pd in the APR of ethylene glycol; the turnover frequency (TOF) of Pd for H<sub>2</sub> production with the incorporation of Fe is 500 times and 150 times higher than those of monometallic Pd and Pt supported on Al<sub>2</sub>O<sub>3</sub>, respectively.[110] After screening over 130 platinum group based catalysts, they reported that PdFe is the most active catalyst with obtained H<sub>2</sub> selectivity of over 95%. This enhancement in catalytic performance is assigned to the superior activity of PdFe for water gas shift of CO to CO<sub>2</sub>/H<sub>2</sub>, which is considered as the rate determining step of the APR reaction. However, a huge number of Fe atoms are needed to modify Pd, which also blocks the surface Pd active sites and reduces the overall H<sub>2</sub> yield.

Tanksale *et al.* reported that the incorporation of a small fraction of Pd into Ni metal also shows a strong synergy effect between the two, giving higher activity and H<sub>2</sub> selectivity than the monometallic Ni, Pd, and even Pt, in the sorbitol APR reaction.[111] Their characterization results indicate that the addition of Pd reduces the CO adsorption strength on the alloy surface, hence enhancing the production of H<sub>2</sub> and CO<sub>2</sub> through the water gas shift (WGS) reaction. In summary, the key steps of APR reaction for biomass molecules appear to lie in the WGS reaction of pre-adsorbed CO. Due to its relatively higher ability in catalyzing WGS reaction than other platinum group elements, Pd exhibits an excellent H<sub>2</sub> selectivity in the APR reaction. The addition of promoter(s) to reduce CO adsorption can further facilitate the activity and selectivity of the Pd containing alloys.



**Scheme 1-5** The parallel pathways of CO and CO<sub>2</sub> production in the MSR reaction.

### 1.2.3 Chemistry of Pd catalysis

By reviewing Pd-based bimetallic catalysis, it is clearly demonstrated the catalytic ability of Pd for a specific reaction can be strongly promoted by the appropriate selection of an alloying element. To rationally design novel catalysts with excellent catalytic properties, it is essential to understand how the insertion of a secondary atom into the Pd lattice influences the catalytic performance. At this stage, the factors affecting the catalytic properties of metals are briefly classified into two categories: (i) the geometric factor and (ii) electronic factor.

### 1.2.3.1 Geometric factor

Geometric factors refer to the elements which are related to the geometry of substance, the atomic packing, lattice parameter, bond length, site occupancy, for instance, ignoring the corresponding electronic influences. With the progressive substitution or decoration of Pd by a secondary element, a series of geometric variations may occur leading to alteration of local chemical environment of Pd: (i) the bond length of Pd-Pd may vary due to a compression or expansion, or even phase transition of the parent lattice; (ii) the size of Pd ensemble decreases with the insertion of modifier atom; (iii) the numbers of corner, edge, low coordinated sites may be reduced as these active sites are favoured by the decoration of a secondary element.[112] These variations play important roles in the adsorption of reactants or intermediates, particularly for bi- or multi- adsorbate(s). Shao *et al.* reported that PdFe shows an excellent catalytic property in the oxygen reduction reaction in the fuel cell, which is superior to monometallic Pd and even the active Pt catalyst. This enhancement is caused by the influence of the Fe atom on Pd-Pd distance as shown in Figure 1-5(a).[113] The activity rises with the decrease in Pd-Pd bond and reaches the peak at a specific ratio of Pd: Fe with the smallest Pd-Pd distance. S. Jones *et al.* reported that Bi atoms dwell specifically on low coordinated sites (corners/edges) in the Pd crystal model.[114] In the decomposition of formic acid, this site blockage suppresses the dehydration reaction ( $\text{HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O}$ ) by decreasing the adsorption site of monodentate formate (the precursor of CO as shown in Figure 1-4) on the corners/edges. This reduces the deactivation of Pd, resulting in a higher rate of formic acid dehydrogenation. Further surface coverage of Bi beyond the corner/edge sites rapidly attenuates the catalytic activity, giving a typical ‘volcano’ response as shown in Figure 1-5(b).

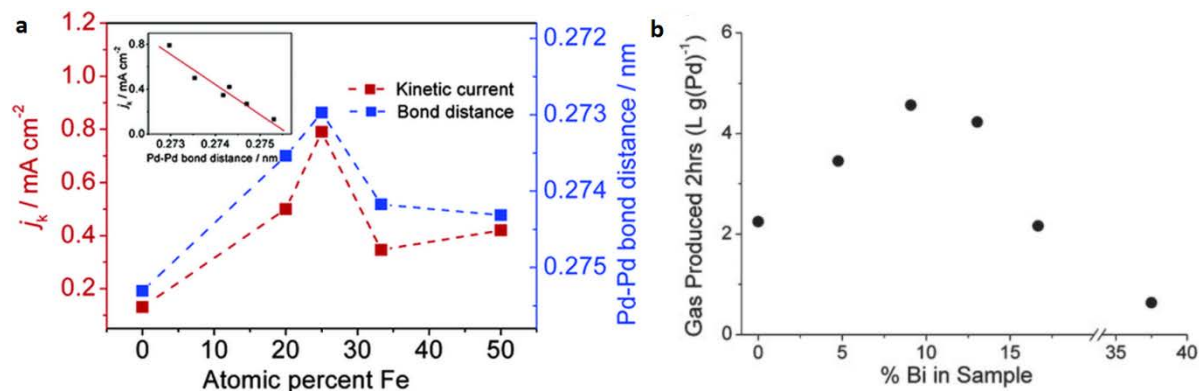


**Figure 1-5** (a) Kinetic current density (per electrochemical area) and Pd-Pd bond distance calculated from XRD data against the concentration of Fe in PdFe/C electrocatalysts treated at 500 °C (from reference 113). (b) Total gas production (2 h) of Bi decorated Pd-PVP with increasing Bi content in the decomposition of formic acid (from reference 114).

### 1.2.3.2 Electronic factor

One of the most fundamental properties of a metal surface is its ability to form bonds with the surrounding atoms and molecules. And this bonding ability determines the catalytic property of the metal surface, because the catalyst surface forms chemical bonds with the reactants. This helps breaking intramolecular bonds and forming new ones during catalysis. [115] Meanwhile, the bonding ability is governed by the electronic structure of the metal as the bonding process involves a redistribution of electron density between the metal and the surrounding atoms or molecules through the overlapping of electron orbitals. All the elements which influence the electronic structure are so called electronic factors which play key roles in catalysis processes. For the transition metals, the electronic structure is mainly described by its *d*-band structure, in terms of its *d*-band center position and *d*-band filling.

It is widely reported that the variation in the *d*-band structure of Pd by the modification of a secondary element eventually influences the catalytic performance. Schlögl *et al.* reported the formation of Pd-Ga heteroatomic bonds in the PdGa bimetallic phase, which created a reduction of density of states at the Fermi edge of the PdGa (the comparison with mono-metallic Pd is shown in Figure 1-6).[116] The alloying with Ga decreases the *d*-band center position of the alloys and eventually reduces the ability of Pd in dissociating hydrogen molecules. Thus this restricts the availability of active atomic hydrogen on the metal surface. As a result, in the hydrogenation of acetylene, PdGa suppresses the total hydrogenation, but strengthens the ethylene selectivity significantly. Chen *et al.* reported the synthesis of a non-surface decoration PdB catalyst by introducing boron (B) atoms into the interstitial octahedral site of Pd lattice. [118] Therefore, no significant geometric variation was observed on the surface of PdB. And the variation of catalytic performance of this PdB catalyst is attributed to the changed electronic structure comparing with the monometallic Pd. The PdB catalyst is found to give ultra-selectivity in a series of selected partial hydrogenation reactions. It outperforms the Lindlar catalysts in the liquid phase owing to the strong electronic perturbation to the parent metal atoms.[118] The density function theory (DFT) calculation shows a broadened and downshifted *d*-band of the alloy when Pd is incorporated with B atoms. The altered *d*-band structure dramatically attenuates the adsorptivity of the metal surface to achieve this ultra-selectivity in partial hydrogenation reaction.

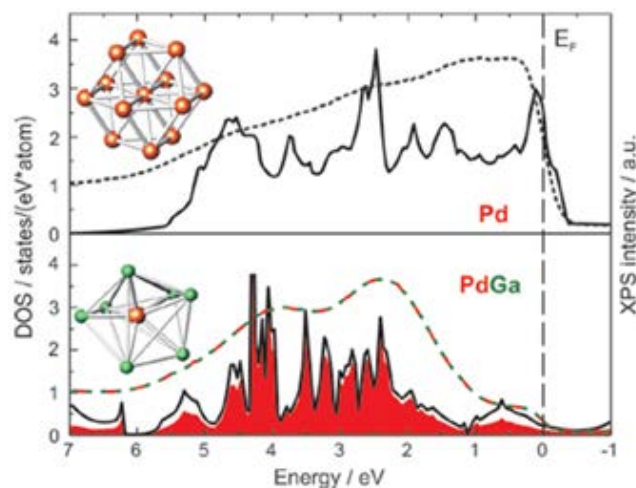


**Figure 1-6** Calculated electronic density of states (DOS) with measured XPS valence band spectra (dashed lines) for elemental Pd (top) and PdGa (bottom) (from reference 116, 117). Pd 4d states of PdGa are shown in red. Note the pronounced changes near the Fermi edge. The insets show the neighbourhood atoms of a Pd atom.

Although the electronic factor and geometric factor can be separated through some extreme synthesis methods, they are tangled with each other in most of the practical catalysts showing synergic or opposite effects. Usually, the insertion of a foreign atom causes a geometric change in the Pd parent lattice, while this geometric change must influence the overlapping of metal d-orbitals which affects the *d*-band structure of the formed bimetallic phase. The variation in electronic structure particularly the *d*-band filling may also result in the change of metal-metal bond length, or even the transition of phase structure, owing to the altered electron repulsion between two neighbor atoms.[119] The convolution of electronic and geometric factors makes the modification mechanism of foreign atoms on Pd catalytic properties complicated. This limits the systematic investigation of geometry and electronic structures of a catalyst, and eventually restricts the rational design of a bimetallic catalyst.

### 1.3 Challenges and objectives

The research of Pd-based catalysis has been paid increasing attention since the 1960's and the outstanding catalytic performance of Pd has been illustrated in a number of reactions as described previously. However, there are still several sharp challenges, concerning facile preparation methods of catalysts, the rational design of novel catalyst, and the investigation of catalytic mechanism.

Noble metal supported on metal oxide is the most widely employed catalyst in industry due to its impressive catalytic ability and stability which are attributed to the SMSI (strong metal and support interaction) phenomenon. The SMSI not only gives a good dispersion but also enhances the catalytic property of a noble metal through the formation of bimetallic NPs. This is due to the decoration of noble metal clusters by the reactive metallic atoms reduced from the underneath oxide support in  $H_2$ . Forming bimetallic NPs is an effective tool to tune and optimize the catalytic ability of Pd. However, the preparation methods, e.g. co-impregnation, thermal decomposition of organo-bimetallic cluster, sequential growth either are difficult to handle or give low dispersion and stability of the bimetallic NPs. Co-reduction of Pd/metal oxide is a facile and mild method in the preparation of well dispersed bimetallic NPs with high stability, but the composition of the Pd-based bimetallic phase is not tunable due to the limited reduction of the support oxide at low temperature. This strongly restricts the further development of Pd/metal oxide catalyst with high catalytic ability.

Presently, most of the commercial catalysts are discovered by numerous screenings of element combinations across the periodic table, which is costly and extremely time consuming. This is due to the lack of understanding in the physiochemical properties of catalysts and catalysis

mechanism(s) of the target reactions. By investigating the modification mechanism of the secondary element on the Pd, it is possible to predict the catalytic properties of the Pd-based bimetallic NPs. Combining with the catalytic mechanism of a specific reaction, a rational design and selection of effective catalyst could be achieved. However this is a very challenging task as it requires not only a thorough understanding of the chemistry, but also powerful characterization techniques.

Currently, more than 80% of the world's energy consumption and production of chemicals is originated from the use of fossil resources, including petroleum, coal, natural gas. With the rapid consumption of these resources and the fast expanding energy demand, the economy driven by these non-renewable energy resources cannot last for a long period. Therefore, a progressive transition to a sustainable economy is urgently demanded. The noble metals, such as Pd with high catalytic ability but with limited reserve, are preferred to be applied into the 'green' catalytic routes which help to increase the energy efficiency of present systems, to reduce the environmental pollution, and more particularly, to diversify energy production and to relieve the dependence on fossil fuels. However, the establishment of new catalytic processes for the utilization of renewable energy resources is extremely difficult as it involves multiple complicated steps including the selection of energy carrier, the design of reaction route, and the development of a highly active catalyst.

Based on the described challenges, this research focuses on three aspects:

- (i) The preparation of extremely small Pd-based NPs with variable modifiers aiming at tuning composition from the reduction of Pd/metal oxide. The key process lies in the controllable reduction of the support at mild reaction conditions.

- (ii) The investigation on the influence of modifier atoms on the physiochemical properties of Pd, and the structure-activity relationship in catalysis processes.
- (iii) The exploration of new synthesis routes for the basic feedstock of daily life through renewable resource utilization, which is considered as the initial step of the transition of economy type. We focus on the Pd catalytic transformation of biomass molecules with -CH(OH)CH(OH)- units into small alcohol molecules which can be used as both fuels and chemical synthesis intermediates.

## **1.4. Overview of the thesis**

Chapter 1: It briefly introduces the background of catalysis including the definition, classification and basic principles. It also reviews the preparation, characterization and recent advances of Pd-based bimetallic catalysts in a series of green catalytic processes. Meanwhile, it lays out the main challenges in Pd-based catalytic processes.

Chapter 2: It introduces the most common analytical tools to characterize solid catalysts developed in this thesis.

Chapter 3: It gives a detailed description of the materials syntheses, characterization methods and catalytic testing processes involved in this thesis.

Chapter 4: It describes a new preparation method of supported bimetallic NPs with high dispersion at adjustable compositions from the co-reduction of noble metal/metal oxide complexes. Also, it investigates the rational control of the reduction behaviour of the catalyst support.

Chapter 5: It describes the syntheses and characterizations of a series of supported PdFe bimetallic NPs. These materials are applied in the hydrogenolysis of biomass derived molecules to small alcohols by selective C-C bond cleavage.

Chapter 6: It involves the synthesis and characterization of a series of Pd-based bimetallic NPs namely, PdFe, PdCo, PdNi and PdZn. It also describes the catalytic performances of these nano-materials in the hydrogenolysis of model biomass molecules, and establishes the structure-activity relationship of Pd-based catalysts.

Chapter 7: It describes the development of a new methanol synthesis route from CO<sub>2</sub> hydrogenation *via* biomass utilization catalyzed by a novel Pd@Zn catalyst at low temperature and pressure.

Chapter 8: It concludes the overall work based on the objectives set for the thesis and proposes perspectives on the future directions of this research area.

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# Chapter 2 Analytical Techniques

## 2.1 Introduction

The characterization of a catalyst has paramount importance in catalysis as the physiochemical properties, particularly surface properties of the catalyst have important impacts on the activity and stability.[1,2] The understanding of these properties shows particular significance in guiding rational design of novel catalysts.

Nowadays, a wide variety of powerful technologies are available to provide information about chemical composition, electronic states, phase structures, surface environments, and local structures of active sites at atomic scale of catalysts. In general, the aspects probed by a single analysis technique are limited. Therefore, a combination of several advanced techniques is usually required to reveal the essence of the active site. This chapter briefly reviews the important analytical tools used throughout this dissertation by presenting their theoretical principles and applications.

The principles of these techniques are based on how catalysts or adsorbed probe molecules on catalysts respond to external stimulations including light irradiation, electron bombardment, heat treatment, etc. The techniques with their applications and irradiation resources are summarized in Figure 2-1. The classified energy regions of various external irradiations are displayed in Figure 2-2.

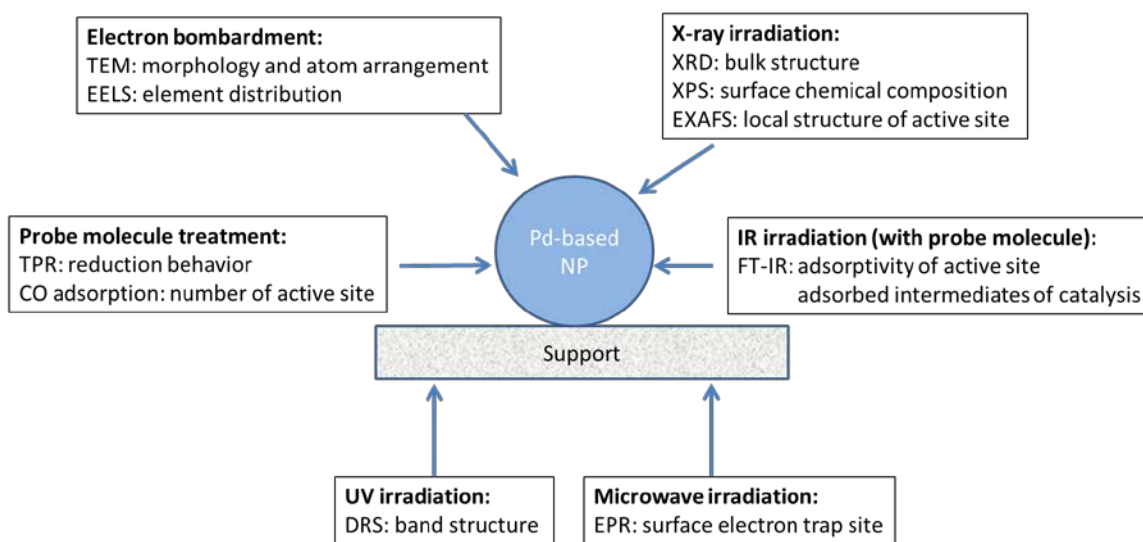


**Figure 2-1** The classification of characterization techniques with their provided information for supported Pd catalysts based on the external simulation resource. (NP, nanoparticle)

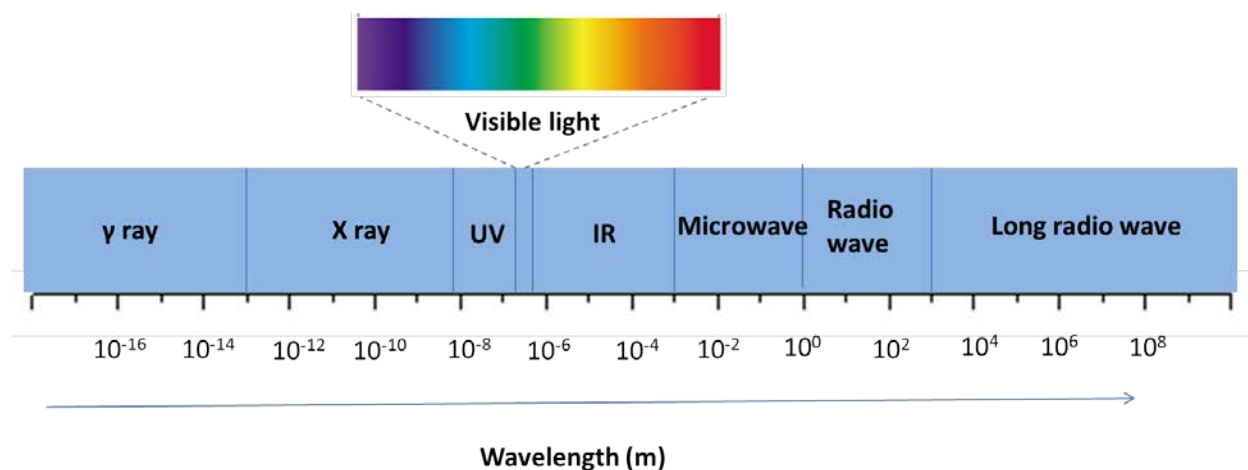


**Figure 2-2** The classified energy regions in term of wavelength for various irradiations.

## 2.2 X-ray Diffraction (XRD)

XRD is one of the most widely used techniques in catalyst characterisation which provides information on crystalline phase, lattice unit cell parameters and gives an indication of crystallite

size by examining the diffraction pattern of a material. The X-ray diffractometer used in this dissertation is displayed in Figure 2-3.



**Figure 2-3** The PANalytical X'Pert Pro X-ray diffractometer at Department of Chemistry, University of Oxford.

An X-ray diffraction pattern is obtained through the constructive interference of the scattered monochromatic X-rays by atoms with periodical arrangement in the lattice as shown in Figure 2-4. Diffraction peaks are observed when Bragg's law is satisfied, which is expressed as:

$$n\lambda = 2d \sin\theta; n = 1, 2, \dots \text{ (Equation 2-1)}$$

where  $n$  is the integer corresponds to the order of reflection;  $\lambda$  is the wavelength of the X-rays (for conventional lab use  $\lambda = 0.154 \text{ nm}$ );  $d$  is the spacing distance of reflecting lattice planes;  $\theta$ , known as the Bragg angle, is the angle between the incoming X-rays and the normal to the reflecting lattice plane.

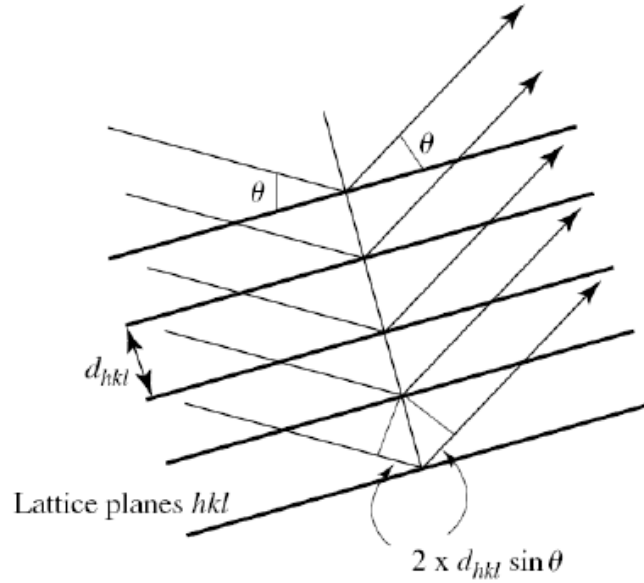


**Figure 2-4** Diffraction of X-rays from crystal lattice planes illustrating Bragg's law. [3]

Using the characteristic peak position of the obtained diffraction pattern, the spacing distance of lattice planes and the lattice parameters can be calculated:

$$n\lambda = 2d \sin\theta \quad (n=1 \text{ for the first order of reflection})$$

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (\text{for orthogonal crystal systems}) \quad (\text{Equation 2-2})$$

where h, k and l are the Miller indices, a, b, c are the lattice parameters and d is the plane spacing.

Another important characteristic of XRD pattern is that the diffraction peaks broaden as the material particle size decreases due to the incomplete destructive interference in scattering directions where the X-rays are out of phase.[4] Therefore, the particle size can be predicted from the width of the diffraction peak using the Scherrer equation:

$$L = K\lambda/\beta\cos\theta \quad (\text{Equation 2-3})$$

where  $L$  is the average diameter of the particles;  $\lambda$  is the wavelength of the incident X-ray;  $\beta$  is the width of a diffraction peak at half the maximum intensity (FWHM) in radians;  $\theta$  is the Bragg angle;  $K$  is a constant which is in the range 0.87-1.00 (it is usually assumed to be 1).

## 2.3 X-ray Photoelectron Spectroscopy (XPS)

XPS is another frequently applied characterization technique based on X-ray irradiation, which provides information on surface chemical composition of a catalyst and determines the oxidation state of individual elements. Upon absorbing the energy of an incident X-ray, a valence or a core electron of the absorbing atom can be ejected from the nucleus with a kinetic energy  $E_k$ :

$$E_k = h\nu - E_B - \varphi \quad (\text{Equation 2-4})$$

where  $E_k$  is the kinetic energy of the ejected electron;  $h$  is Planck's constant;  $\nu$  is the frequency of the incident X-ray;  $E_B$  is the binding energy of the ejected electron with respect to the Fermi level of the sample;  $\varphi$  is the work function of the spectrometer. The relationship of the four parameters is illustrated in Figure 2-5.

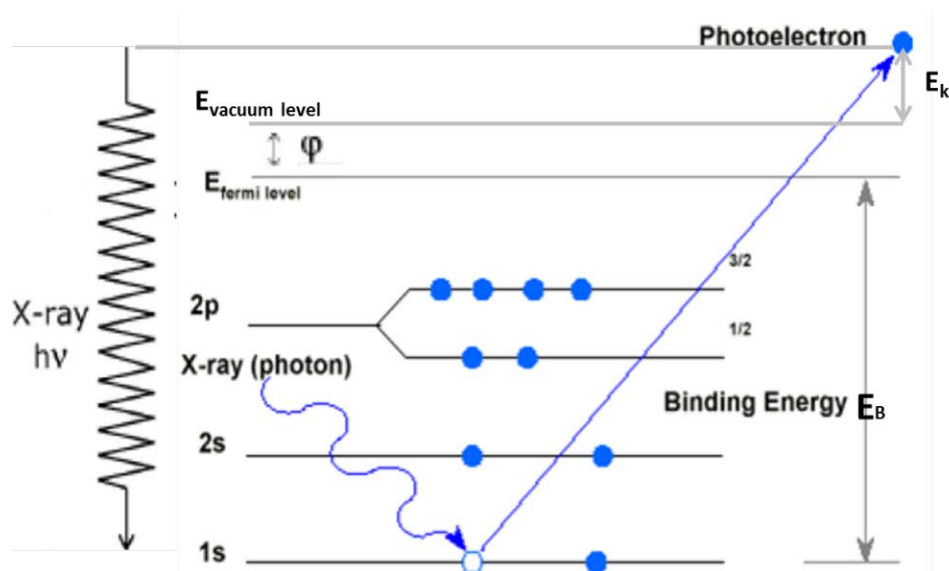


**Figure 2-5** Illustration of electron ejection stimulated by X-ray absorption [4]

The kinetic energy ( $E_k$ ) of the photoelectron is an experimental value measured by the spectrometer, which depends on the wavelength of the employed X-rays and is therefore not an intrinsic property of the material. [5] In contrast, the binding energy of the electron ( $E_B$ ) is a characteristic which identifies the parent element of the electron and also reflects the oxidation state of the element.[6] Thus, the XPS spectrum is usually plotted using the intensity of the ejected electrons ( $N(E)$ ) versus their binding energy ( $E_B$ ). The total number of detected electrons at a certain binding energy region is proportional to the amount of the parent element. Based on the signal peak areas of elements normalized by the relevant sensitivity factors, XPS can be used to analyse the chemical composition of a catalyst in a quantitative way. [7] Although X-rays penetrate deeply into the material, most of the ejected electrons with kinetic energy are captured again by the parent element and only a small fraction of surface photoelectrons can escape from the material and be detected by the spectrometer. Thereby, the chemical composition provided by XPS is assigned to the surface or near surface area of the catalyst which reflects the information of active site more precisely than other bulk analysis techniques.

Although  $E_B$  is an intrinsic property, it varies slightly with the oxidation state of element which is determined by the coordination environment. Therefore, XPS is also widely used to detect the binding energy variation of an element in bimetallic catalysts and to deduce the electronic interaction of between the two elements.

## 2.4 Extended X-ray Absorption Fine Structure (EXAFS)

EXAFS is a powerful technique based on X-ray irradiation providing information on local structures of the absorbing atoms. Thus, it is widely employed to reveal the essence of the active sites and has attracted increasing attention in the catalytic mechanism investigation.

EXAFS is part of X-ray absorption spectroscopy (XAS) as shown in Figure 2-6 where XAS is the measurement of the X-ray absorption coefficient  $\mu$  of a material as a function of X-ray energy, where  $\mu$  is defined as:

$$\mu = -\ln\left(\frac{I_t}{I_0}\right)/X \quad (\text{Equation 2-5})$$

( $I_0$  is the intensity of X-ray light shone on the sample;  $I_t$  is the intensity of X-ray light transmitted through the sample;  $x$  is the thickness of the sample).

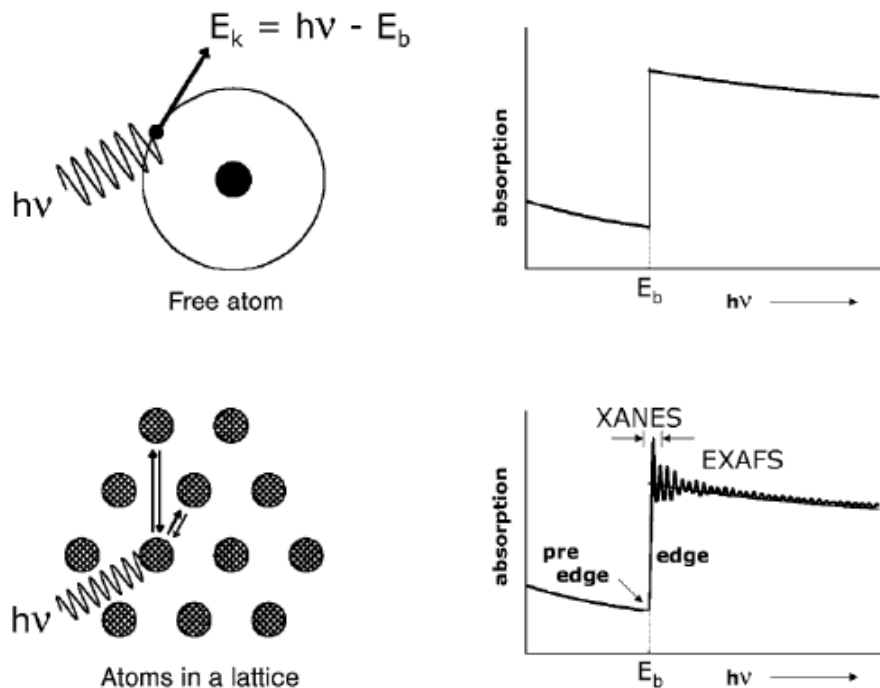


**Figure 2-6** Absorption of X-rays as a function of X-ray energy  $E = h\nu$  by a free atom (top) and by atoms in a lattice (bottom) and their corresponding XAS. (XANES: X-ray absorption near edge spectroscopy.) [8]

When the incident X-ray energy matches the binding energy of an electron of one element within the sample, the absorption coefficient  $\mu$  increases dramatically, causing an absorption edge in XAS. The position of the absorption edge usually reflects the oxidation state and the electronic configuration of the absorbing element. After the absorption edge, the excited electrons escape from the nucleus with kinetic energy, and are likely to be backscattered by the neighbour atoms of the absorbing atom and interfere with the forward ejected ones. This interference causing oscillation in XAS after the absorption edge is called EXAFS, which depends on the type of scattering atoms around the absorbing one and the distance between them. The EXAFS function,  $\chi(k)$ , is extracted from XAS by removing the absorption spectrum of the free atom and the

approximately parabolic background as shown in Figure 2-6 where  $k$  is the wave number of the ejected electron, which can be calculated from the kinetic energy as:

$$k = \frac{2\pi}{h} \sqrt{2m_e E_{kin}} = \frac{2\pi}{h} \sqrt{2m_e (h\nu - E_B)} \quad (\text{Equation 2-6})$$

where  $h$  is Planck's constant;  $m_e$  is the mass of an electron;  $E_{kin}$  is the kinetic energy of the photoelectron;  $\nu$  is the X-ray frequency;  $E_B$  is the binding energy of the ejected electron.

The model of EXAFS function  $\chi(k)$  is quite complicated, which has been compiled into some professional software for EXAFS data processing. All the EXAFS data presented in this dissertation are fitted by IFEFFIT 1 with Horae packages 2 (Athena and Artemis). By curve fitting of EXAFS data, the chemical environment of the absorbing atom at atomic scale can be derived including the type of surrounding atoms, the coordination number and the bond distances of neighbour atoms.

## 2.5 Transmission Electron Microscopy (TEM)

TEM is a powerful technique used to observe the catalyst at nano-scale directly, which reveals information about the finest details of the internal structure of the material, for example, particle size, morphology and atom arrangement. Theoretically, the principle of TEM is similar to that of an optical microscope only electrons instead of visible photons are employed as light source and electromagnetic lenses are used to focus the electron beam in TEM instead of optical lenses in an optical microscope. The structure of TEM is illustrated in Figure 2-7.

Briefly, a primary electron beam of high intensity generated from the electron gun is accelerated to high energy to produce electrons with a de Broglie wavelength much smaller than typical interatomic spacing. The high speed electron beam firstly passes through a condenser to produce

parallel rays, which then impinge on the specimen. The transmitted electron beam through the specimen is then refocused and expanded through sets of projector lenses onto the phosphor screen or a charge coupled device (CCD).

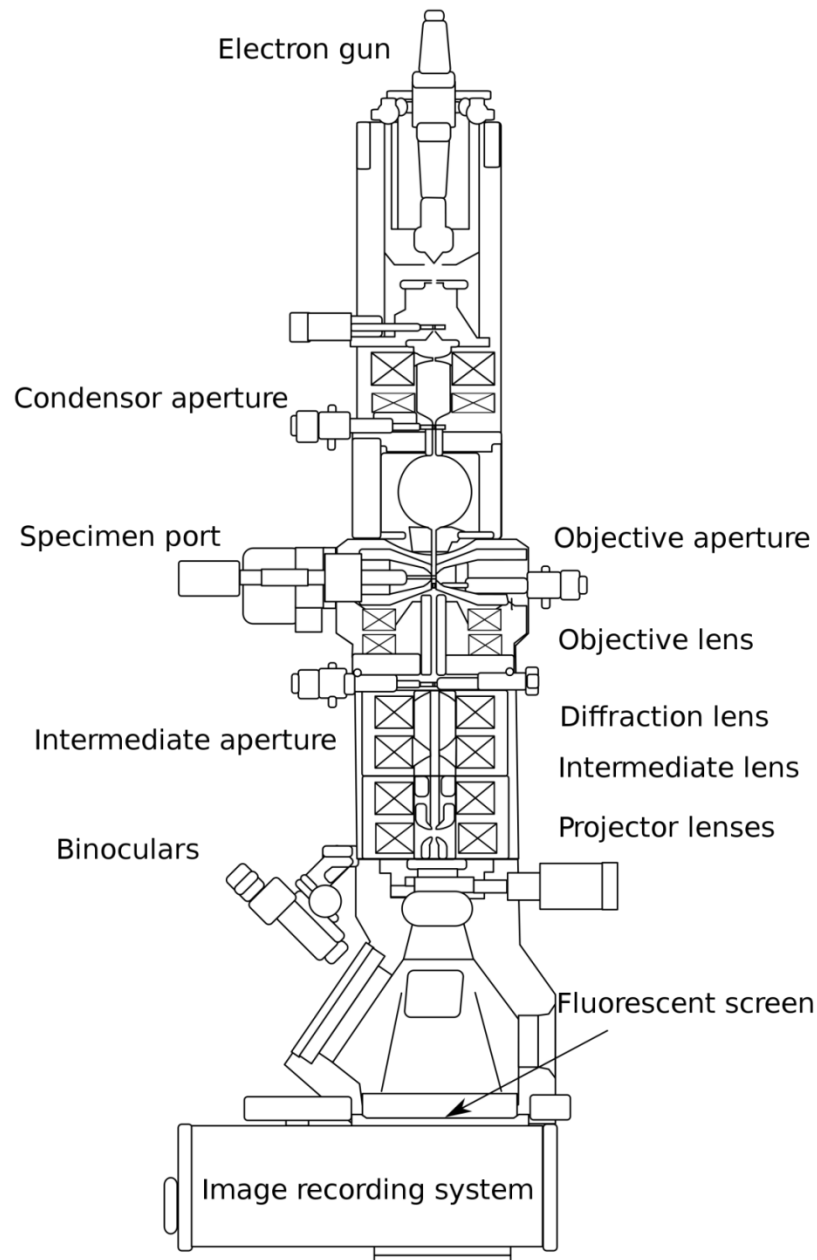


**Figure 2-7** The typical structure of a TEM machine.[3]

According to the Rayleigh criterion, the generally accepted criterion for the minimum resolvable distance between two points of equal brightness, the resolution of a microscope is defined as:

$$\delta_d = \frac{0.61\lambda}{n \sin\beta} \quad (\text{Equation 2-7})$$

where  $\lambda$  is the wavelength of the radiation;  $n$  is the refractive index of the view medium;  $\beta$  is the semi-angle of collection of the magnifying lens. As a result, the resolution of TEM is determined by the wavelength of the electron. Typical operating conditions of a TEM instrument are 100 to 200 keV electrons ( $\lambda = 2.5$  to  $3.7$  pm),  $10^{-6}$  mbar vacuum, corresponding to a resolution of  $0.3$  nm (with a magnification of  $3 \times 10^5$  to  $10^6$ ) which is thousands of times smaller than the smallest resolvable object in a light microscope.

The most common operation mode of TEM is the bright field imaging mode, which refocuses electrons being transmitted through the sample or slight scattered. The dark areas of the image represent areas with fewer electrons being transmitted either due to thicker regions of the sample or heavier atoms, as heavy atoms with large nuclei scatter electrons more than the lighter atoms which decrease the transmitted electrons. [9]

## **2.6 Electron Energy Loss Spectroscopy (EELS)**

Due to the same irradiation source (electron), an EELS part is usually attached to a TEM machine. Thus, TEM and EELS are often combined together for catalyst characterization. In EELS, the specimen is exposed to a beam of electrons with a known, narrow range of kinetic energies. Some of the electrons will undergo inelastic scattering by the atoms in a specimen, which means that they lose energy and have their paths slightly and randomly deflected. The

amount of energy loss can be calculated by the measurement of outgoing electron energy and interpreted in terms of what causes the energy loss.

Inelastic interactions between the incident electrons and the atoms in a specimen can cause phonon excitations, inter- and intra-band transitions, plasmon excitations, inner-shell ionizations, and Cherenkov radiation in the sample. Atom ionization with some inner-shell electrons removed is the most common process causing energy loss of the incident electron beam. The value of energy loss equals the binding energy of the removed electron. The process of the atom inner-shell ionization by the incident electron is displayed in Figure 2-8. Due to the characteristic of binding energy, EELS is particularly useful for identifying and quantifying the elements of a material. Coupled with TEM, EELS is a powerful technique to map the elemental distribution of a specimen.

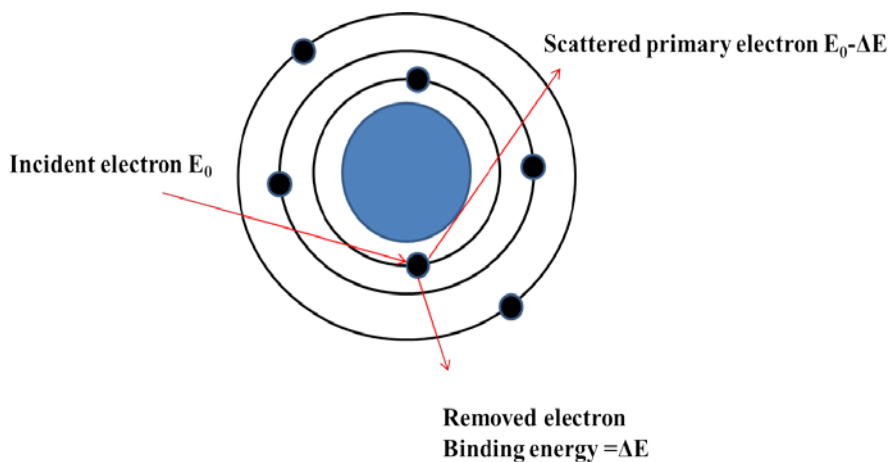


**Figure 2-8** A brief model of inelastic scattering of incident electrons by the atoms in a specimen

Owing to the diversity of the inelastic interaction between the incident electron beam and the atom electrons in the specimen, EELS is capable of giving other structural and physical information about the sample. Besides the chemical composition, band structure, surface

property and chemical bonding of the specimen can also be provided by EELS based on variable excitation modes of the atom electron by incident electrons.

## **2.7 Diffuse Reflectance Spectroscopy (DRS)**

With ultraviolet-visible (UV-Vis) light as the irradiation resource, UV-Vis DRS is one branch of ultraviolet-visible spectroscopy. The principle is based on electronic transitions of molecules or solid material from the ground state to the excited state by absorbing light energy in the UV-Vis region. In catalysis, some typical semi-conductors with clear separation of valence and conduction bands, for instance ZnO, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> *etc*, are widely employed as supports for noble metals. And their band structures usually influence the catalytic performance through the strong metal support interaction (SMSI). UV-Vis spectroscopy is a powerful and accurate method to characterize the band gap of a semi-conductor. When the energy of incident light matches the band gap value, the valence electrons of a semi-conductor can be excited to jump across the band gap and occupy the conduction band causing a sharp absorption edge in the UV-Vis spectroscopy. The excitation process is shown in Figure 2-9. The information on this excitation process is contained in the transmitted and diffusely reflected light by the specimen. Due to the significant thickness, poor dispersion in solvent or the dark color of solid sample, the incident light can be totally absorbed, scattered, reflected leading to almost no or very weak transmitted light being detected. Thus, DRS with the measurement of diffusely reflected light by the specimen is more frequently used to characterize the electronic structure of the semi-conductor support instead of UV-Vis absorption spectroscopy. The process of reflectance and transmission of UV-Vis light by a solid sample are shown in Figure 2-10.

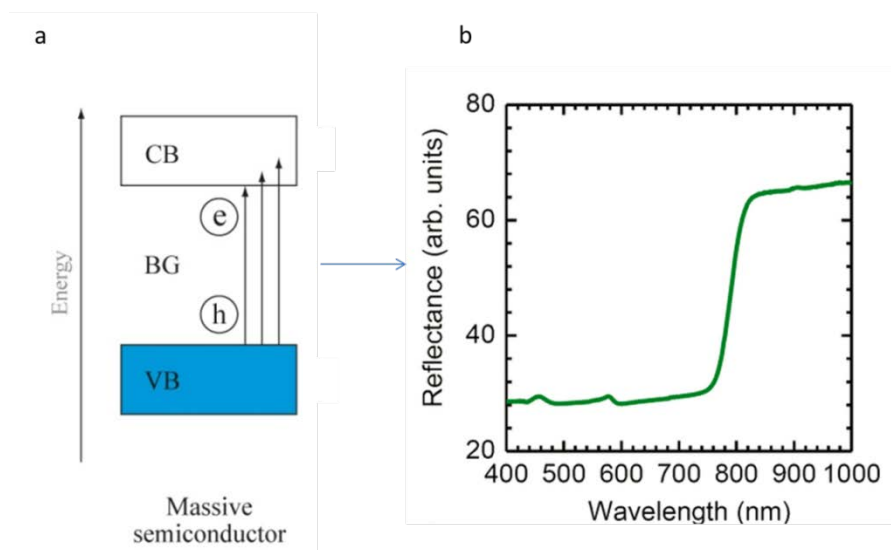


**Figure 2-9** (a) Excitation process, and (b) typical DRS curve of semi-conductor. (VB, valence band; CB, conduction band; BG, band gap, e and h represent the excited electron and hole)

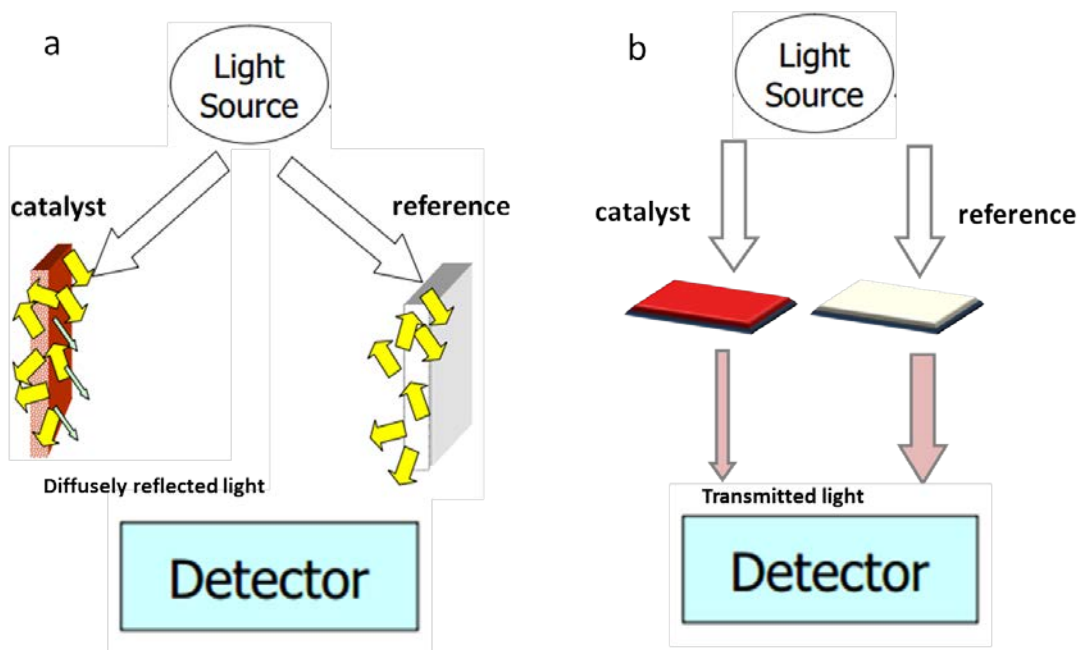


**Figure 2-10** Simplified processes of (a) diffuse reflectance, and (b) transmission of UV-Vis light on solid sample.

DRS is recorded as a curve of reflectance coefficient versus wavelength of the UV-Vis light. Reflectance coefficient is defined as  $R_{\infty}$  equaling to  $I_s/I_r$  ( $I_s$  and  $I_r$  represent the intensity of reflected light by the specimen and reference, respectively). Usually, KBr is employed as a blank reference and the samples are diluted in KBr with a concentration of 3 wt%.

Band gap ( $E_g$ ) values of semiconductor nanocrystals can be calculated from DRS using the Tauc equation: [10, 11]

$$(h\nu * F(R_{\infty}))^{\frac{1}{n}} = A(h\nu - E_g) \quad F(R_{\infty}) = \frac{(1-R_{\infty})^2}{2R_{\infty}} \quad (\text{Equation 2-8})$$

where  $h\nu$  is the energy of light (in eV),  $F(R_{\infty})$  is the remission function which is calculated from the reflectance coefficient,  $A$  is the proportionality constant and  $E_g$  is the band gap value (in eV). The value of  $n$  depends of the nature of the electronic transition being investigated. For a direct allowed transition  $n = 1/2$ , whereas for an indirect allowed transition  $n = 2$ . For a direct band gap semi-conductor, the intercept on x-axis of the linear portion of  $(F(R_{\infty})*h\nu)^2$  versus  $h\nu$  plot (at the band gap absorption edge) gives the value of  $E_g$ .

## 2.8 Photoluminescence (PL) Emission Spectroscopy

Photoluminescence (PL) of material can be defined as the emitted radiation after its excitation by absorbing photon energy from an external source.[12] As stated in section 2.7, in the excitation process of a semi-conductor, the electrons in the valence band (VB) jump across the band gap and occupy the conduction band (CB) temporarily, which generates holes in VB accordingly. Usually, the excited electrons drop back to the VB rapidly and recombine with the holes leading to an emission of energy equaling to the value of band gap (band to band luminescence). If the excitons are stabilized by some surface defects or impurities with energy levels close to the

bands edge, the recombination rate of electrons and holes will decrease accompanied by a life-time extension of the excitons. This delayed recombination usually gives an emitted radiation at longer wavelength (so called deep level luminescence) as illustrated in Figure 2-11.

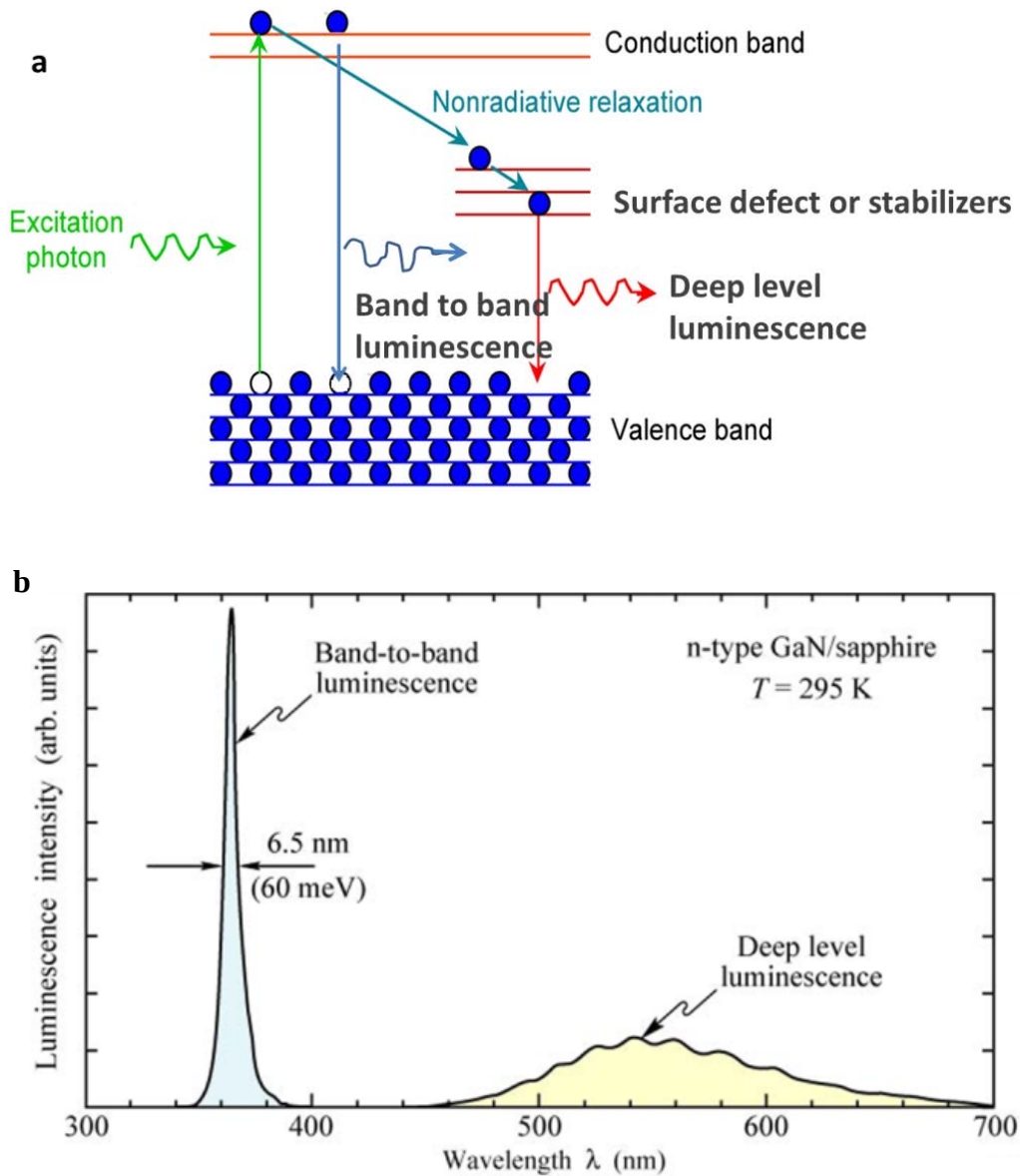


**Figure 2-11** (a) Illustration of the recombination of excitons on semiconductor with emitted irradiation, and (b) typical PL spectroscopy of GaN semi-conductor which involves both band to band luminescence and deep level luminescence.[13]

Thus, PL spectroscopy is a useful analytical technique for probing exciton behavior in semiconductor nano-crystals and also provides information of band structure and surface state of the solid materials. PL spectroscopy measurements can either be time-resolved (emitted photon density over time) or steady state (emitted photon density as a function of emission wavelength). Steady state PL measures the emission intensity (perpendicular to excitation) at a single wavelength of excitation ( $\lambda_{\text{ex}}$ ) across a range of energies, yielding a fluorescence spectrum. This spectrum reflects information of the band structure and defects, impurities, adsorbed species, etc. on the surface of a specimen. Time-resolved photoluminescence (TRPL) is obtained via time-correlated single photon counting (TCSPC) after a short burst of excitation (using a pulsed laser). In each TCSPC, the time between sample excitation by a pulsed laser and the arrival of the emitted photon at the detector is measured. TCSPC requires a defined “start”, provided by the electronics steering the laser pulse or a photodiode, and a defined “stop” signal, realized by detection of single-photon with sensitive detectors. The set-up of TRPL based on TCSPC unit is shown in Figure 2-11a. The measurement of TCSPC is repeated many times to account for the statistical nature of the fluorophore emission. The arrival times of emitted photons are sorted into a histogram that plots the occurrence of emission over time after the excitation pulse as shown in Figure 2-11b.

The decay of the emitted photon intensity with time after the excitation can be expressed as:

$$I_t = I_0 \sum A_i \exp(-t/\tau_i) \quad (\text{Equation 2-9})$$

where  $I_0$  is the intensity at time zero (upon excitation);  $A_i$  is amplitude of component and  $\tau$  is the lifetime which is usually used to indicate the life length of excitons reflecting the recombination rate of excited electrons and holes. In an ideal case (e.g. a crystalline absorber with passivated

surfaces), TRPL decays would be single-exponential (linear when plotted on log-linear scale). In contrast, in the case of nano-material with an imperfect interface, defective surface or adsorbed impurity, the approximation of multi-exponentials is needed. Also a series of  $\tau$  can be obtained which implies the existence of the variable recombination mechanism of excitons.

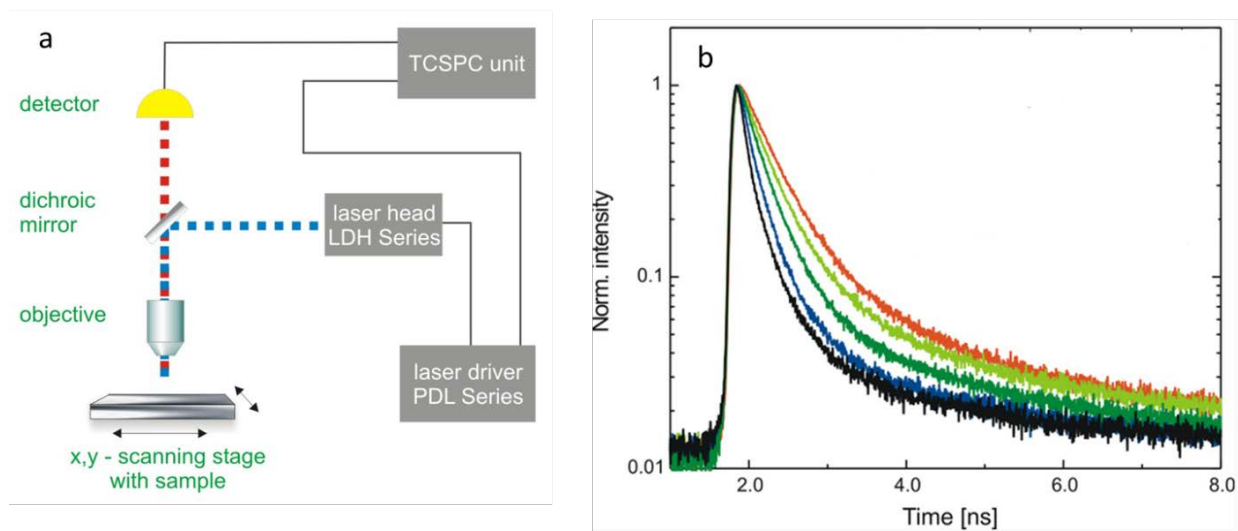


**Figure 2-12** (a) Instrument set-up of the time-resolved PL spectroscopy, and (b) typical time-resolved decay profile.

## 2.9 Fourier Transform Infrared (FTIR) Spectroscopy

Molecules possess discrete rotational and vibrational energy levels. A vibrational transition can occur by absorbing infrared light, in particular with a wavenumber of ( $200\text{--}4000\text{ cm}^{-1}$ ) as shown in Figure 2-13a.

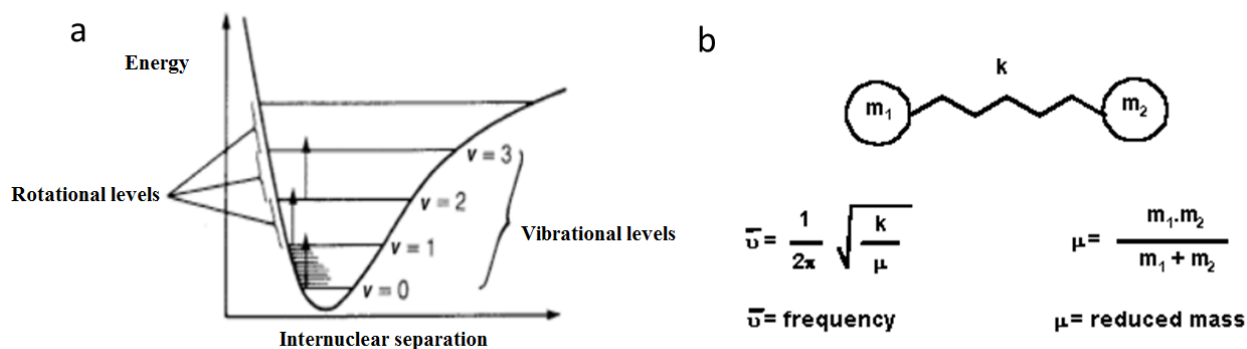


**Figure 2-13** (a) Discrete vibrational energy levels of molecule, and (b) model of a simple Harmonic Oscillator.[14a]

If each chemical bond in molecule is regarded as a Harmonic Oscillator as shown in Figure 2-13b, the energy of a vibrational level of this pair of atoms can be described as (based on the solution to the Schrödinger equation of Harmonic Oscillator):

$$E_V = \left(V + \frac{1}{2}\right) h\nu_0 \quad (\text{Equation 2-10})$$

where  $V$  is the quantum number ( $V = 1, 2, \dots$ ) and  $\nu_0$  is the characteristic vibration frequency of the Harmonic Oscillator,  $E_v$  is the energy of vibrational level with quantum number  $V$ . Usually, transitions between the neighbour vibrational levels ( $v \Rightarrow v+1$ ) with  $\Delta E = h\nu_0$  are strong. Thereby, an IR absorption peak is frequently observed at frequency equaling to  $\nu_0$  in the spectroscopy (an IR spectrum is a graph of infrared light absorbance (or transmittance) on the vertical axis against frequency or wavelength on the horizontal axis). The Harmonic Oscillator frequency of the two atom chemical bond  $\nu_0$  is characteristic and described as:

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \mu = \frac{m_1 \cdot m_2}{m_1 + m_2} \quad (\text{Equation 2-11})$$

where  $m_1$  and  $m_2$  are the masses of atoms in the chemical bond and  $k$  is the force constant which is proportional to the bond strength between the atoms. Thus, the IR spectroscopy is a sensitive analytic tool to characterize the strength of chemical bonds within a molecule. Through the identification of IR peaks, the structure of a molecule can be identified.

Although IR spectroscopy is a vibrational spectroscopy, not all vibration modes cause IR absorption. A change in dipole moment in the molecule during the vibration process is essential for the IR absorption.

In a catalysis process, when the reactant molecule is adsorbed on the catalyst surface, the related chemical bonds will be altered based on the interaction of adsorbed molecule with the catalyst, which shifts the IR absorption peak positions. Thereby, with the approaching of simple probe molecules, for instance CO, NO etc., information about electronic and geometric structure of the catalyst surface which dominates the interaction with the probe molecules can be provided. On the other hand, by stimulating the reaction atmosphere in an IR sample cell with loaded catalyst, the catalytic process can be traced by *in situ* IR spectra collection as IR is sensitive enough to detect the reaction intermediates.

A typical setup of an FTIR spectrometer is illustrated in Figure 2-14. A source of incoherent infrared light is produced using a glowing black body. The light is directed into a Michelson interferometer made up of a stationary mirror, a beam splitter and a moving mirror. The light is split by the beam splitter and ideally 50% of the light is refracted towards the stationary mirror and 50% is transmitted towards the moving mirror. When the light recombines at the beam splitter, it interferes with itself, after which it is directed to the sample, then focused onto the detector (Figure 2-14). The raw absorption signal is detected as an interferogram at many

discrete positions of the moving mirror, which will be Fourier transformed to understand the light energies absorbed by the sample. FTIR spectrometers are mechanically simple with only one continually moving part, and the instrument is internally calibrated against a helium-neon laser. [14b]

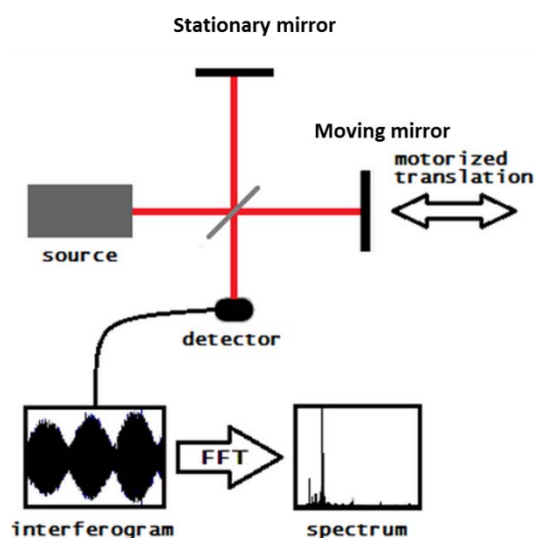


**Figure 2-14** Brief illustration of typical setup of an FTIR spectrometer. (FFT represents fast Fourier transform)

## 2.10 Electron Paramagnetic Resonance (EPR)

EPR is a typical technique for studying materials with unpaired electrons. The basic concepts of EPR are analogous to those of nuclear magnetic resonance (NMR), but electron spins are excited instead of the spins of atomic nuclei. Every electron has a magnetic moment and spin quantum number  $s = 1/2$ , with magnetic components  $m_s = +1/2$  and  $m_s = -1/2$ . Without exposure to the external magnetic field, the energy levels of a free electron with  $m_s = +1/2$  or  $-1/2$  are degenerate. In contrast, in the presence of the external magnetic field, the energy level splits which is governed by the parallel or antiparallel alignment of electron magnetic moment to the field:

$$E = m_s g_e \mu_B B_0 \quad (\text{Equation 2-12})$$

where  $E$  is the energy level of the unpaired electron,  $B_0$  is the strength of magnetic field,  $\mu_B$  is the Bohr magneton,  $g_e$  is so called  $g$ -factor. Therefore, the separation between the lower and the upper state is  $\Delta E = g_e \mu_B B_0$  for unpaired free electrons, which is directly proportional to the strength of magnetic field, as shown in the diagram below.

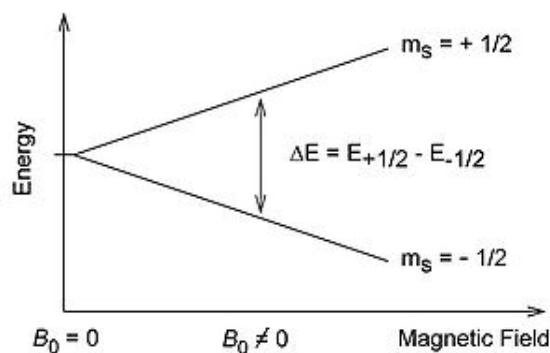


**Figure 2-15** Illustration of energy splitting of unpaired electron with stimulation of external magnetic field.

Without external irradiation, the numbers of electrons in the two separated energy levels follow the Maxwell-Boltzmann distribution. While upon exposure to microwaves with energy  $h\nu$  equaling to  $\Delta E = g_e \mu_B B_0$ , the unpaired electron lying in the lower energy level can be excited into higher energy level by absorbing a photon. An EPR spectrum can be generated by either varying the frequency of incident microwaves on a sample while fixing the strength of magnetic field, or doing the reverse. Then through the position of absorption signal, the  $g$  factor can be calculated. For a free electron,  $g_e$  equals to 2.00 but the observed value is different for localized electrons. For an unpaired electron in radical or trapped on a crystal surface, the effective

strength ( $B_{\text{eff}}$ ) of the external magnetic field ( $B_0$ ) experienced by the detected electron is modulated by its surrounding atoms with local magnetic field, which is thereby written as:

$$B_{\text{eff}} = (1 - \sigma)B_0 \quad (\text{Equation 2-13})$$

Thus, the EPR signal should be observed at:

$$h\nu = g_e \mu_B B_0 (1 - \sigma) \quad (\text{Equation 2-14})$$

where  $g = g_e(1-\sigma)$ ,  $\sigma$  is the total effect of all the surrounding atoms.

Therefore, the observed  $g$  value calculated from an EPR spectrum varies from 2.00, indicating the characteristic chemical environment of the localized electron.

EPR is a very sensitive technique for the detection and identification of free radicals and paramagnetic centers. Thus, it is widely used in samples from basic organic and inorganic compounds to complex biomolecules, such as proteins. Here, we briefly introduce the application of EPR in the characterization of semi-conductors. For these materials, the valence electrons can be excited temporarily to the empty conduction band by thermal heating or by absorbing natural light. These excited electrons should be delocalized on a well-defined crystal surface until they combine with the corresponding holes. However, for a catalyst with particle size of nano-region, there are a number of defects, interstitial sites or adsorbed impurities at the surface or interface of multi-components, due to the poor crystallization of nano-particles. These sites can trap the excited electrons momentarily causing a signal in the EPR spectra. The intensity of the signal and the calculated value of the  $g$  factor usually reflect surface state of the catalyst.

## 2.11 Temperature Programmed Reduction (TPR)

Most of the metal/metal oxide catalysts need a pre-reduction process for the generation of active sites before they are used in catalysis. TPR is a technique to investigate the reduction behavior of materials. The diluted reductive gas, usually  $H_2$  or  $CO$ , is used to interact with the specimen loaded in a quartz tube by passing a continuous gas stream under a user pre-defined temperature ramp. The variation of probe molecule concentration in the gas flow is monitored *in situ* by a thermal conductivity detector (TCD) at elevated temperatures. The illustration of a TPR instrument setup is shown in Figure 2-16. Two reductive gas streams with same composition are supplied. One is taken as the reference flowing into the TCD detector directly (in the reference line of Figure 2-16) and the composition of this gas stream is considered to be constant. The other one passes through and interacts with the specimen before it arrives at the detector (in the sample line of Figure 2-16). The intensity of TCD signal is proportional to the difference in composition of the two gas streams. Thereby, the variation of probe molecule concentration in the sample line is recorded at increasing temperature with reference to the gas stream skipping the specimen. This reflects the reduction process of the sample.

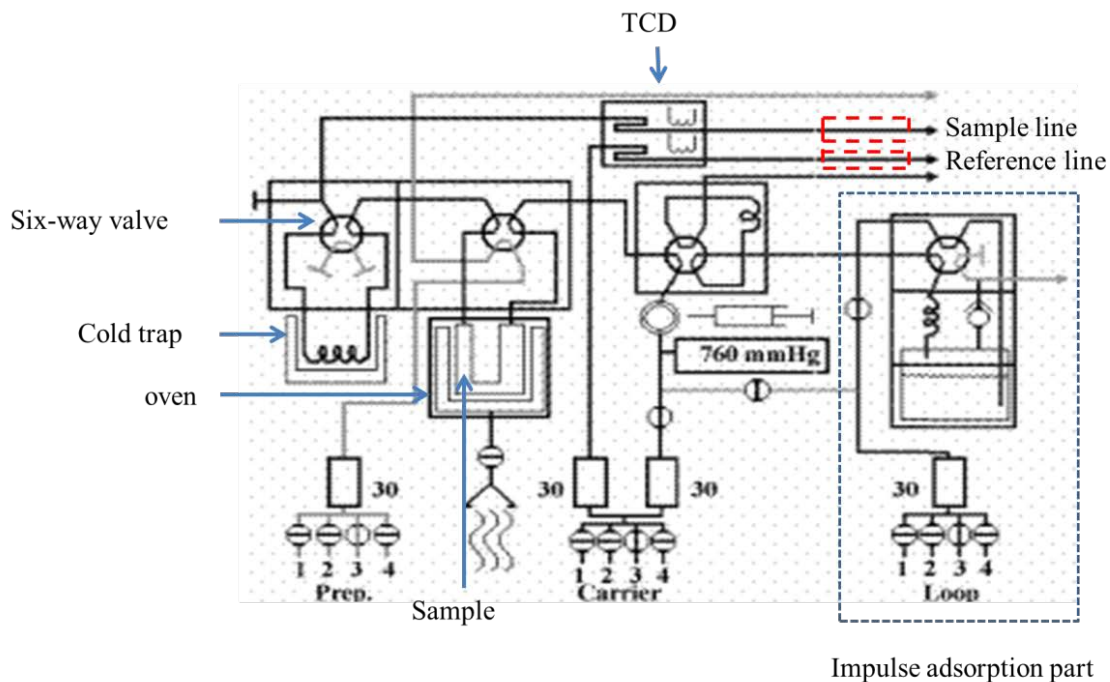


**Figure 2-16** Setup of a typical TPR instrument.

In a typical measurement, a catalyst is sandwiched between two layers of quartz wool in a quartz tube, which is placed inside the external quartz tube where it is merged with the stainless steel holder and sealed by a rubber o-ring (Figure 2-17).

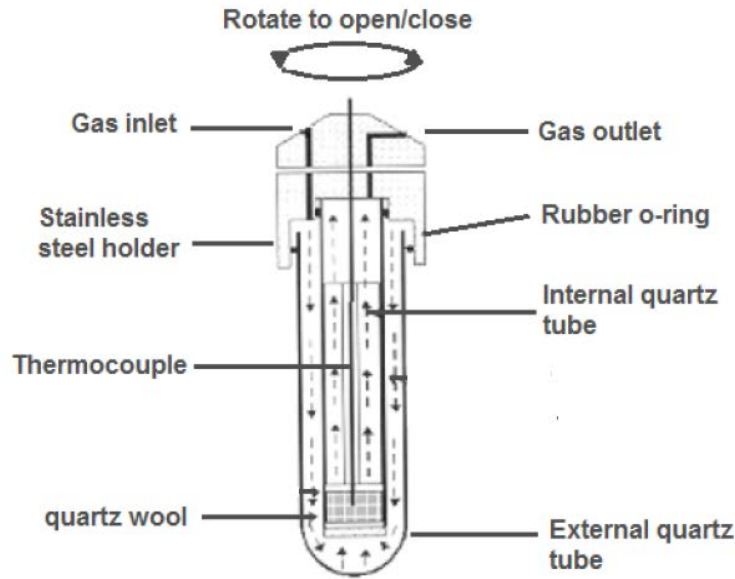


**Figure 2-17** Diagram for the TPR reactor assembly. [15]

TPR analysis can provide information on the reduction behavior of the specimen including the reduction temperature, the amount of the reducible species, and the activation of the reduction process. The reduction temperature can be observed from the TPR curve. The integration of TCD signal versus temperature gives the total uptake of  $H_2$  (after an accurate calibration) which is useful in inducing the number of reductive sites and the corresponding reduction degree. In addition, the recorded reduction temperature in the TPR curve is dependent on the ramp rate of temperature as following:

$$2\ln T_m - \ln \beta = \frac{E_a}{RT_m} + A \quad (\text{Equation 2-15})$$

where  $T_m$  is the temperature at the optimum of reduction peak recorded in TPR curve;  $\beta$  is the temperature ramp rate;  $E_a$  is the activation energy;  $R$  is the ideal gas constant; and  $A$  is a constant.

When TPR is run at a variable temperature ramp, the activation energy of the corresponding reduction process can be calculated from the slope of  $2\ln T_m - \ln \beta$  against  $1/T_m$ .

Overall, this technique is particularly useful and powerful in investigating the reduction behavior of a catalyst.

## 2.12 CO Chemisorption

Chemisorption is a frequently used technique to characterize the metal phase of a catalyst. It provides quantitative information, such as metal surface area, metal dispersion and metal crystallite size, and makes it possible to correlate the catalyst properties with its catalytic performance. Chemisorption is a type of adsorption which involves a chemical reaction between the surface and the adsorbate. New chemical bonds are generated at the adsorbent surface, thus only mono-layer of the adsorbate can be chemisorbed on the metal surface and the chemisorption is strong enough to resist some external stimulation, including vacuum and gas sweeping. CO is mostly used in determining the number of metal active site for Pd-based catalysts due to its typical linear adsorption mode on Pd site with a 1:1 ratio. Thus, the amount of chemisorbed CO equals number of metal active sites.

During a chemisorption experiment, the sample is first reduced in hydrogen and then evacuated to retrieve the active metal phase. In the volumetric method, known amounts of carbon monoxide are dosed. It is subsequently adsorbed at different partial pressures, resulting in a chemisorption isotherm. The isotherm measurement is repeated after applying an evacuation step at the analysis temperature which removes weakly adsorbed species on the catalyst. The difference between the two isotherms represents the chemically bonded reactive gas and can be used to calculate the

active metal surface area. Combined with the information on metal loading, the metal dispersion and the average metal crystallite size can also be calculated.

## 2.13 Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

ICP-AES is a common technique used for the detection of metal elements in materials. It is a type of emission spectroscopy that uses inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at characteristic wavelengths of a particular element. [16, 17] The intensity of this emission indicates the concentration of the element within the sample. The principle of this technique is displayed in Figure 2-18.

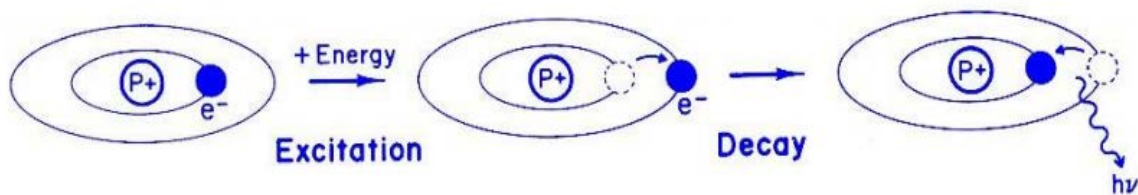


**Figure 2-18** Excitation and relaxation process of detected atom in ICP-AES. [18]

As the name suggests, ICP-AES is composed of two parts: the ICP and the optical spectrometer. ICP excites the atoms in a specimen, while AES detects the emitted characteristic energy.

ICP-AES analysis requires aqueous sample. When the sample solution is introduced into the spectrometer, it becomes atomized into a mist-like cloud. This mist is carried into the argon plasma with a stream of argon gas. The plasma (ionized argon) produces temperatures close to

7,000 °C, which thermally excites the outer-shell electrons of the elements in the sample. [19]  
This process happens in the ICP part.

The relaxation of the excited electrons as they return to the ground state is accompanied by the emission of photons of light with an energy characteristic of the element. Because the sample contains a mixture of elements, photons of variable light wavelengths are emitted simultaneously. Through the analysis of each wavelength, the detected elements can be identified. To quantify the concentration of each element, it is most common to select a single wavelength (or a very few) for a given element. The intensity of the photon emitted at a chosen wavelength is proportional to the amount (concentration) of that element in the analyzed sample. And the detected elements are quantified one by one.

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# Chapter 3 Experimental Methods

## 3.1 Synthesis procedure

### 3.1.1 Synthesis of supported PdFe and RhFe bimetallic NPs with variable composition

The PdFe or RhFe bimetallic clusters were produced through the reduction of PdO/Fe<sub>2</sub>O<sub>3</sub> or Rh<sub>2</sub>O<sub>3</sub>/Fe<sub>2</sub>O<sub>3</sub> complexes which was synthesized by a precipitation method. Zn(II) was added in the growth process of Fe<sub>2</sub>O<sub>3</sub> support to modulate the reduction of Fe ions to Fe(0) from the support in the following pre-reduction. This dictated the ratio of Pd: Fe in the bimetallic clusters.

First, solutions of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (50 mL) and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (200 mL) in various concentrations were prepared. Next, 10 mL Na<sub>2</sub>CO<sub>3</sub> solution (1 M, 10.6 g Na<sub>2</sub>CO<sub>3</sub> in 100 mL deionized water) was slowly added into the 50 mL Zn(NO<sub>3</sub>)<sub>2</sub> solution to generate a white suspension of Zn(OH)<sub>x</sub>. The obtained mixture was then added drop-wise into the 200 mL Fe(NO<sub>3</sub>)<sub>3</sub> solution to form a reddish gel-like solution. The pH of the final gel was adjusted to 4 by adding 1 M Na<sub>2</sub>CO<sub>3</sub> solution. Then, the reddish gel was added slowly into a solution of Rh(NO<sub>3</sub>)<sub>3</sub> (0.05 wt% Rh) or Pd(NO<sub>3</sub>)<sub>2</sub> (0.05 wt% Pd), and the pH of this mixture was adjusted to 9 by further adding 1 M Na<sub>2</sub>CO<sub>3</sub> solution. The solutions of Rh(NO<sub>3</sub>)<sub>3</sub> (0.05 wt% Rh) and Pd(NO<sub>3</sub>)<sub>2</sub> (0.05 wt% Pd) were diluted from the 0.66 g commercial nitrate salt solution of Johnson Matthey (15 wt% Rh or Pd) into 200 mL deionized water. The pH value of the solution was monitored by a pH meter (Mettler Toledo PHQ-180-050W). The final mixture was stirred overnight and the solid product was harvested by centrifugation. The solid was rinsed with copious amount of water in order to remove any residual sodium ion before it was dried in an oven at 80 °C for 24 hours. All the dried samples were calcined at 300 °C in air for 2 hours. The

pre-reduction of the samples were done in a 3-neck flask with a  $\text{H}_2$  flow of  $30 \text{ mL min}^{-1}$  at  $250^\circ\text{C}$  for 1 hour.

To control the composition of the produced bimetallic NPs, the amount of added zinc nitrate and iron nitrate were varied among the samples and summarized in Table 3-1.

**Table 3-1** The amount of added precursors of a series of zinc modified  $\text{PdO/Fe}_2\text{O}_3$  or  $\text{Rh}_2\text{O}_3/\text{Fe}_2\text{O}_3$  before the pre-reduction (the loading of Pd or Rh is 5 wt%).

| Sample | Mass of added<br>$\text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (g) | Mass of added<br>$\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (g) |
|--------|--------------------------------------------------------------------|--------------------------------------------------------------------|
| 1      | 0.00                                                               | 10.41                                                              |
| 2      | 1.18                                                               | 7.90                                                               |
| 3      | 1.48                                                               | 7.50                                                               |
| 4      | 2.29                                                               | 6.40                                                               |

### 3.1.2 Synthesis of supported PdCo and PdNi bimetallic NPs with variable composition

Supported PdCo bimetallic NPs were prepared by the reduction of cobalt blended  $\text{Pd/Fe}_2\text{O}_3$ . Iron oxide was used as main support of Pd particles and cobalt nitrate was added to act as the precursor of metallic Co. The synthesis procedure is described as follows: 1.55 g  $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 7.59 g  $\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were dissolved in 50 mL and 200 mL deionized water, respectively. 10 mL  $\text{Na}_2\text{CO}_3$  solution (1 M) was dropped to the solution containing Co precursor. The obtained purple suspension was then dropped into the 200 mL  $\text{Fe(NO}_3)_3$  solution and the pH of the final gel was adjusted to 4 by the  $\text{Na}_2\text{CO}_3$  solution. The reddish gel was added into 200 mL  $\text{Pd(NO}_3)_2$  (0.05 wt% Pd) solution and the pH of this mixture was adjusted to 9. The final mixture was left stirring overnight and the solid product was harvested by centrifugation. The solid was rinsed with a copious amount of water in order to remove any residual sodium ion

before it was dried in an oven at 80 °C for 24 hours. The dried samples were calcined at 300 °C in air for 2 hours. The pre-reduction of the samples was done in a 3-neck flask with a H<sub>2</sub> flow of 30 mL min<sup>-1</sup> at 250 °C for 1 hour, which is the same as that of PdFe and RhFe samples

The concentration of Co in the final Pd-based bimetallic NPs can be tuned by varying the amount of cobalt precursor. The amounts of precursors added in the synthesis of supports are shown in Table 3-2.

**Table 3-2** The amount of added precursors of a series of cobalt blended PdO/Fe<sub>2</sub>O<sub>3</sub> samples before the pre-reduction.

| Sample | Mass of added<br>Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O (g) | Mass of added<br>Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O (g) |
|--------|---------------------------------------------------------------------------|---------------------------------------------------------------------------|
| 1      | 0.00                                                                      | 9.61                                                                      |
| 2      | 1.55                                                                      | 7.59                                                                      |
| 3      | 2.36                                                                      | 6.54                                                                      |
| 4      | 3.50                                                                      | 5.06                                                                      |
| 5      | 5.05                                                                      | 3.04                                                                      |

The synthesis of PdNi is similar with that of PdCo only 1.48 g Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 7.50 g Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were employed as precursors. The precipitation method and the following thermal treatment is exactly the same with that of PdCo samples.

### 3.1.3 Synthesis of supported PdZn bimetallic NPs

The PdZn catalyst is produced by a typical co-precipitation process of PdO/ZnO followed by a pre-reduction in H<sub>2</sub> atmosphere. [1] 0.66 g Pd(NO<sub>3</sub>)<sub>2</sub> solution (15 wt% Pd, from Johnson Matthey) and 7.40 g zinc nitrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) were dissolved in 400 mL deionized water. 1 M Na<sub>2</sub>CO<sub>3</sub> solution was dropped to precipitate Zn<sup>2+</sup> and Pd<sup>2+</sup> until the pH of the mixture reached

9. The final mixture was stirred overnight. The crystalline product was collected by centrifugation and was washed extensively with deionized water to remove any residual sodium ions. The final product was dried in an oven at 80 °C for 24 hours. The final product is calcined and pre-reduced under the same conditions with PdFe, PdCo, PdNi samples.

### **3.1.4 Synthesis of Pd@Zn bimetallic nano-structures**

The Pd@Zn core-shell structure was prepared by the controllable reduction of PdO/ZnO-CdSe nano-composite. The ZnO-CdSe support is synthesized by a sequential growth of CdSe and ZnO. CdSe particles are obtained through the reaction of  $\text{Na}_2\text{SeSO}_3$  and  $\text{Cd}(\text{NO}_3)_2$ . The  $\text{Na}_2\text{SeSO}_3$  aqueous solution was prepared by refluxing 0.79 g Se powder in an aqueous  $\text{Na}_2\text{SO}_3$  solution (4.0 g  $\text{Na}_2\text{SO}_3$  in 100 mL deionized water) at 80 °C overnight. 0.64 g  $\text{Cd}(\text{NO}_3)_2$  and 14.70 g sodium citrate ( $\text{HOC}(\text{COONa})(\text{CH}_2\text{COONa})_2 \cdot 2\text{H}_2\text{O}$ ) were dissolved into 100 mL water to form a solution. This solution was then mixed with freshly prepared 0.1 M  $\text{Na}_2\text{SeSO}_3$  (100 mL) into a flask and heated in water bath at 60 °C for 15 minutes. The red precipitate was collected by centrifugation and the solid product was extensively washed, after which the supernatant was decanted and discarded. The growth of ZnO rod was carried out by Zeng's method. [2] 1.487 g zinc nitrate [ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] and 6.000 g NaOH were dissolved in 10 mL deionized water (the molar ratio of  $\text{Zn}^{2+}$  to  $\text{OH}^-$  was 1:30). Variable amounts of previously produced CdSe particles were dispersed into 100 mL ethanol to prepare ZnO-CdSe supports with variable ratios (the amounts of added CdSe in a series of samples are displayed in Table 3-3). This ethanol suspension was added to the solution containing Zn precursor. 5 mL ethylenediamine (EDA) was also added into the mixture, which was then transferred to a 250 mL covered plastic container. The system was kept at room temperature under constant stirring until the red mixture turned white. The white crystalline product was then collected by centrifugation and was washed with deionized water and

pure ethanol. The final product was dried in an oven at 60 °C for 12 hours. The loading of 5 wt% Pd onto above synthesized support was achieved by the impregnation method; the ZnO-CdSe support was immersed into a Pd(NO<sub>3</sub>)<sub>2</sub> ethanol solution (3 wt% Pd) and the mixture was kept stirring at 50 °C until the ethanol solvent was evaporated. The harvested powder was calcined at 400 °C for 2 hours. The pre-reduction of the samples were done in a 3-neck flask with a H<sub>2</sub> flow of 20 mL min<sup>-1</sup> at 250 °C for 2 hours.

**Table 3-3** The amounts of added CdSe in synthesis of a series of ZnO-CdSe supports.

| Sample                 | 1    | 2    | 3    | 4    |
|------------------------|------|------|------|------|
| Mass of added CdSe (g) | 0.00 | 0.03 | 0.09 | 0.12 |

## 3.2 Catalytic test

### 3.2.1 Hydrogenolysis of biomass derived molecules

The hydrogenolysis reactions were carried out in liquid phase using a 160 mL autoclave fitted with a glass liner. In a typical experiment, 30 mL of substrate solution and freshly reduced catalyst were loaded into the reactor inside a glove box. The reactor was flushed with pure (99.9%) hydrogen gas 6 times to remove any trace amount of air. The autoclave was pressurized to 50 bar with hydrogen gas at room temperature, after which it was heated up to a certain temperature to allow the reaction to proceed with constant stirring (200 rpm). The substrates employed in this thesis include ethylene glycol (EG, 5.0 wt%), 1,2-propanediol (1,2-PD, 5.0 wt%), 1,2-butanediol (1,2-BD, 5.0 wt%) and glycerol (1.0 wt%).

After the allotted reaction time, the autoclave was cooled down to -60 °C in a dry ice/acetone bath. Here, the gas phase was analyzed by a Perkin Elmer Autosystem XL Arnel Gas

chromatography fitted with FID-Methanator in order to determinate the concentrations of CO, CH<sub>4</sub> and CO<sub>2</sub> in the reaction products. The column was carbowax 80-100 mesh packed and N<sub>2</sub> gas was employed as a mobile phase (18 psi). The oven was programmed at an initial temperature of 180 °C for 0.5 minute and then heated to 250 °C at a rate of 40 °C min<sup>-1</sup>. The final temperature of 250 °C was held for 10 minutes.

The liquid phase was analyzed by a Perkin Elmer 200 series HPLC (high-pressure liquid chromatography) equipped with a refractive index detector. 0.60 mL of 58 mM sucrose solution (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>) was added as an external standard to determine the concentrations of substrate and liquid product after the reaction. The products were separated on a 300 mm × 7.8 mm Aminex HPX-87H ion exclusion column at an oven temperature of 35 °C. The mobile phase was 0.025 M sulfuric acid (prepared with Fisher HPLC grade water) at a flow rate of 0.6 mL min<sup>-1</sup>. The carbon balance of this typical catalytic batch reaction of over 95% was ensured.

### 3.2.2 The hydrogenation of CO<sub>2</sub> to methanol

Catalyst tests in hydrogenation of CO<sub>2</sub> were carried out in Wuhan University (Wuhan, China) by using a fixed bed micro-reactor as shown in Figure 3-1. Catalyst weight of 0.1 g sandwiched by two layers of quartz wool was loaded in a steel tube (12.7 mm outside diameter) which can be fitted into the instrument. Before each test, the catalyst was pre-reduced at 250 °C for 2 hours under the H<sub>2</sub> flow (20 mL min<sup>-1</sup> at stp). After the pre-reduction procedure, CO<sub>2</sub>/H<sub>2</sub> reaction mixture with molar ratio of 1:2.8 was fed at a rate of 30 mL min<sup>-1</sup> at stp (stp=standard temperature and pressure; P=101.3 kPa, T=298 K) through the catalyst bed. The products were analyzed *in situ* by a connected gas chromatography (GC) equipped with a thermal conductivity detector (TCD). Pure H<sub>2</sub> was employed as the mobile phase with a flow rate of 20 mL min<sup>-1</sup>. The temperatures of the oven and TCD detector in the GC were set to 120 °C and 80 °C. The

temperature and pressure at the catalyst bed can be set and operated accurately, which allows the investigation of kinetic and the optimization of catalyst.



**Figure 3-1** The employed fixed bed micro-reactor for CO<sub>2</sub> hydrogenation at Wuhan University, Wuhan, China

### 3.3 Catalyst characterizations

#### 3.3.1 Powder X-Ray Diffraction (PXRD) and Synchrotron X-ray Diffraction (SXRD)

X-ray diffraction data of the samples were collected on a Philips PW1729 diffractometer operating in Bragg-Brentano focusing geometry and using Cu K<sub>α</sub> radiation ( $\lambda = 1.5418 \text{ \AA}$ ) from a generator operating at 40 kV and 30 mA. The step size and scan rate are set at 0.004°, 0.000225°/s, respectively.

Samples were prepared by placing a layer of dry powdered sample onto an aluminum sample holder and this holder gives characteristic diffraction pattern as shown in Figure 3-2.

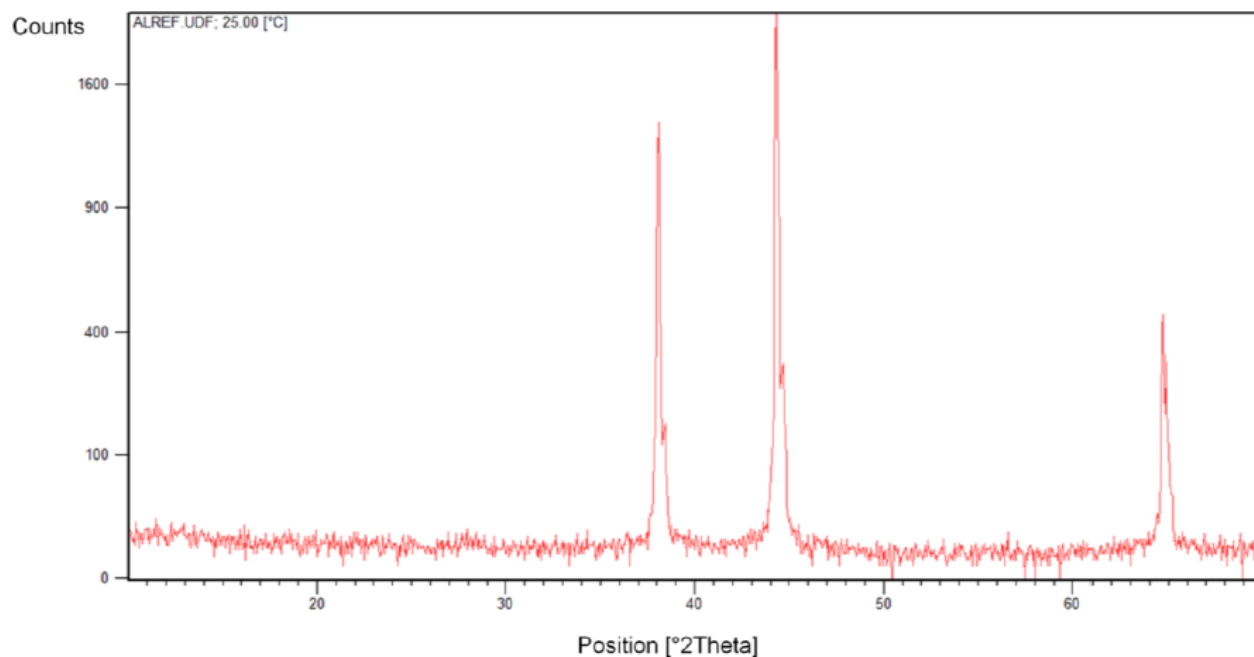


**Figure 3-2** XRD pattern of blank aluminum sample holder.

SXRD was performed on Beamline I11 at Diamond light Source (UK) with the assistance of Professor Chiu Tang. Optimized at 15 keV using a low bandpass monochromator (cryogenic-cooled double-Si(111)-crystals), the diffraction instrument receives a high brightness X-ray beam from an in-vacuum undulator. It has multi-analyzing crystals (MAC) detectors and a 90° aperture position sensitive detector (PSD) to achieve the high angular resolution with negligible instrumental contribution. SXRD patterns of selected samples were collected with the PSD using a wavelength of 0.826172(1) Å calibrated from a Si pattern of a standard powder (SRM640c). More technical details describing the Beamline can be found in the article by Thompson *et al.* (2011) [3]. Powder samples were loaded in borosilicate glass capillaries (0.5 mm diameter).

### **3.3.2 X-ray Photoelectron Spectroscopy (XPS)**

Samples were analyzed by a Thermo V. G. Scientific ESCALAB 250 using Al  $K_{\alpha}$  (1486.6 eV) X-ray source. A hemispherical analyzer was employed for the detection of electrons. To avoid the re-oxidation of pre-reduced samples, the loading process into the XPS instrument was finished in a glove bag connected to the entrance of the machine with  $N_2$  protection. The resulting spectra were analyzed using Peak Fitting software and sample charging was corrected using C 1s at 284.5 eV as a reference setting.

### **3.3.3 Extended X-ray Absorption Fine Structure (EXAFS)**

EXAFS measurements at Pd K-edge (24530 eV) and Rh K-edge (23230 eV) were performed on Beamline B18 at Diamond Light Source, UK, to obtain information about the local structure of the noble metals (the nearest-neighbor inter-atomic distances and coordination number). Also, it was used to estimate the composition of metal particles. The experiments were finished with assistance of Dr. Andrew Dent and Dr. Anna Kroner. The Diamond installation comprises a 3 GeV electron storage ring with typical currents of 200 mA. B18 is a bending magnet beamline which has been designed to deliver monochromatic X-rays in the energy range of 2 to 35 keV. A Si(311) double crystal monochromator was used for energy selection with a resolution of 1 eV. X-ray absorption spectroscopy data was collected at ambient temperature in transmission mode using optimized ionization chambers as detectors. Fluorescence spectra were acquired using  $I_0$  and a high count rate fluorescence 9-element Ge detector.

The samples were loaded between two layers of quartz wool in a plastic tube with diameter of 6 mm. The tube was fulfilled with argon gas and the loading process was finished in a glove box with argon protection.

The EXAFS data analysis was performed using IFEFFIT 1 with Horae packages 2 (Athena and Artemis). All spectra were calibrated with Pd and Rh foil as a reference to avoid small energy shifts of the nano-catalyst. The amplitude parameter was obtained from EXAFS data analysis of Pd or Rh foil with a known coordination number equaling to 12, which was used as a fixed input parameter in all fits to allow coordination number (CN) refinement.

In this work, we have only performed a first shell data analysis under the assumption of a single scattering. The curve-fitting analysis was done in  $k^3$  space with a range of 2-12. The quality of the curve fitting is measured by the R-factor.

### **3.3.4 Transmission Electron Microscopy (TEM) and Electron Energy Loss Spectroscopy (EELS)**

TEM images and EELS spectra were obtained using a JEOL 2021F microscope operating at 200 kV equipped with a post-column Gatan imaging filter (GIF-Tridium) at Fudan University, Shanghai, China. The samples were prepared by placing a drop of nano-particle-ethanol suspension onto a carbon-coated copper grid, and allowing the solvent to evaporate.

### **3.3.5 Diffuse Reflectance Spectroscopy (DRS)**

The DRS data of solid sample was collected on a Perkin-Elmer LAMBDA 750S UV/Vis/NIR spectrometer. Samples were prepared by thoroughly grinding sample powder (*ca.* 3 mg) and dry KBr (*ca.* 300 mg) together until a well dispersed and finely ground mixture was achieved. The resulting solid mixture was compressed into a sample pellet (diameter *ca.* 13 mm, thickness *ca.* 3 mm) using an applied force of 10 tonnes for 90 seconds. The sample disk was placed into the beam path by mounting the disk (in place of the standard Teflon reflecting disks) in the

integrating sphere compartment of the spectrometer. A pellet of KBr was prepared as standard reference.

### **3.3.6 Photoluminescence (PL) emission spectroscopy**

To probe excitation dynamics (in particular lifetimes of the electrons and holes) and also investigate the surface state of catalysts, time-resolved photoluminescence (TRPL) and steady photoluminescence (PL) measurements have been conducted on a commercial Ti: Sapphire regenerative amplifier laser system (800 nm, 40 fs, 1 kHz, 3.5 mJpulse<sup>-1</sup>) and home built spectrometers. The experiments were finished with the assistance of Dr. Wai-ming Kwok and Dr. Chensheng Ma in Hong Kong Polytechnic University.

300 nm and 280 nm excitation pulses generated by the one-photo absorption (OPA) were applied for TRPL and static PL, respectively. The measurements were done with samples in the solid state. Both TRPL and PL signals were collected by a spectrograph and detected with a liquid nitrogen cooled CCD detector. All the measurements were conducted at room temperature and atmospheric pressure.

The samples were prepared by placing drops of nanoparticle ethanol suspension onto a quartz plate, and allowing the solvent to evaporate until a layer of sample was deposited on the plate.

### **3.3.7 Fourier Transform Infrared (FTIR) spectroscopy**

*In situ* FTIR spectra were employed to investigate the catalytic mechanism of CO<sub>2</sub> hydrogenation. The data were collected on a Tensor 27 spectrometer (Bruker) equipped with CaF<sub>2</sub> windows. Spectra were obtained by collecting 64 scans with a resolution of 4 cm<sup>-1</sup>. The measurement was finished in transmission mode and the data is presented in absorbance units.

Powders of samples (mixture of 10mg sample and 10mg gamma-Al<sub>2</sub>O<sub>3</sub>) were prepared into pellets and loaded onto a sample holder ( the holder is a supported stainless ring with the sample exposed to IR light source). The sample was then flushed with 5% H<sub>2</sub>/Ar (20 mL min<sup>-1</sup>) for 10 minutes and then reduced in 1 hour at 250 °C. After the pre-reduction treatment, vacuum condition was put on the cell until the pressure is lower than 1×10<sup>-6</sup> bar and then backgrounds were recorded at 50 °C, 100 °C , 150 °C , 200 °C , 250 °C .

After collecting backgrounds, a mixture of CO<sub>2</sub>/H<sub>2</sub> (3:100, 20 mL min<sup>-1</sup>) was passed through the reduced sample pellet and then the *in situ* FTIR spectra were collected at 50 °C, 100 °C , 150 °C , 200 °C , 250 °C with the sample maintained at each temperature for 10 minutes.

### **3.3.8 Electron Paramagnetic Resonance (EPR)**

EPR were recorded on a Bruker EMX spectrometer using an Eleksys probe head. Calculation of the spin number was based on a reference powder of Cu(II)TPP with 1 spin per molecule.

### **3.3.9 Temperature Programmed Reduction (TPR)**

TPR was used to investigate the reduction behavior of catalysts and estimate the composition of produced metal particles. The data was collected on a Thermo-Quest TPRO 110 instrument. Inside the TPR quartz tube, 0.01 g of the calcined catalyst sample was sandwiched between two layers of quartz wool with a thermocouple placed in contact with the top layer quartz wool. The TPR tube was then inserted into the instrument for a pre-treatment (helium run through the TPR tube at 10 mL min<sup>-1</sup> at a temperature ramp of 10 °C min<sup>-1</sup> from 40 °C up to 150 °C, then is held for 5 minutes before cooling). The helium pre-treatment cleaned the catalyst surface by removing the adsorbed ambient gas molecules. After the pre-treatment, a reduction treatment (5% H<sub>2</sub> in

argon flow through the TPR tube at 20 mL min<sup>-1</sup> at a temperature ramp of 10 °C min<sup>-1</sup> from 40°C up to 800 °C) was carried out, in order to observe the reduction process of the catalysts.

### **3.3.10 CO chemisorption**

The chemisorption uptake of CO was measured to determine the number of Pd active site per gram of catalyst with the ratio of Pd: CO=1. The data were measured on a Micromeritics ASAP 2020 (M+C) analyzer. The samples were pre-reduced at 250 °C and evacuated for 1 hour at 250 °C to ensure a high surface cleanliness. An initial isotherm was measured in an adsorbate pressure range of 100-600 Torr at a precisely controlled temperature of 35 °C. Subsequently, evacuation at 35 °C for 30 minutes was conducted to remove the weak reversibly adsorbed CO molecules before measuring another repetitive isotherm under the same conditions as the initial one. The difference between the repetitive and initial isotherm is denoted as the uptake of irreversibly chemisorbed CO on catalysts.

### **3.3.11 Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES)**

ICP-AES was performed on an IRIS Intrepid II XSP spectrometer. The samples were dissolved in aqua regia and then diluted in deionized water. The final concentration of the sample was controlled in a range of 10-100 ppm.

## Appendix

The manufacture information of the chemicals employed in this thesis is displayed in Table 3-4.

**Table 3-4** The manufacture information of the employed chemicals

| <b>Chemical</b>                                                    | <b>Manufacture company</b> | <b>Purity (%)</b> |
|--------------------------------------------------------------------|----------------------------|-------------------|
| <b>Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O</b>              | Sigma-Aldrich              | 98%               |
| <b>Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O</b>              | Sigma-Aldrich              | >98%              |
| <b>Na<sub>2</sub>CO<sub>3</sub></b>                                | Sigma-Aldrich              | >99%              |
| <b>Rh(NO<sub>3</sub>)<sub>3</sub></b>                              | Alfa Aesar                 | 15 wt% Pd         |
| <b>Pd(NO<sub>3</sub>)<sub>2</sub></b>                              | Alfa Aesar                 | 15 wt% Rh         |
| <b>H<sub>2</sub></b>                                               | BOC                        | 99%               |
| <b>Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O</b>              | Sigma-Aldrich              | >98%              |
| <b>Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O</b>              | Sigma-Aldrich              | >98.5%            |
| <b>Se</b>                                                          | Aldrich                    | >99.99%           |
| <b>Na<sub>2</sub>SO<sub>3</sub></b>                                | Sigma-Aldrich              | >98%              |
| <b>Cd(NO<sub>3</sub>)<sub>2</sub></b>                              | Aldrich                    | 98%               |
| <b>HOC(COONa)(CH<sub>2</sub>COONa)<sub>2</sub>·2H<sub>2</sub>O</b> | Aldrich                    | 99%               |
| <b>NaOH</b>                                                        | Sigma-Aldrich              | >98%              |
| <b>Ethylenediamine</b>                                             | Fluka                      | >99.5%            |
| <b>Ethylene glycol</b>                                             | Sigma-Aldrich              | >99.8%            |
| <b>1,2-propanediol</b>                                             | Sigma-Aldrich              | >99.5%            |
| <b>1,2-butanediol</b>                                              | Fluka                      | >98.0%            |
| <b>Glycerol</b>                                                    | Sigma                      | >99%              |
| <b>Acetone</b>                                                     | Sigma-Aldrich              | >99%              |
| <b>Sulphuric acid</b>                                              | Aldrich                    | 99.99%            |
| <b>CO<sub>2</sub></b>                                              | BOC                        | >99%              |
| <b>Ethanol</b>                                                     | Sigma-Aldrich              | >99.8%            |
| <b>HCl</b>                                                         | Sigma                      | 36.5%-38.0%       |
| <b>HNO<sub>3</sub></b>                                             | Sigma-Aldrich              | 70%               |

## References:

- [1]. S. Liu, K. Takahashi, M. Ayabe, *Catalysis Today*, **2003**, 87, 247–253.
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- [3]. S. P. Thompson, J. E. Parker, J. Marchal, J. Potter, A. Birt, F. Yuan, R. D. Fearn, A. R. Lennie, S. R. Street and C. C. Tang, *J. Synchrotron Rad.* **2011**, 18, 637-648.

# Chapter 4 A New Class of Tunable 'Hetero-junction Support' for the Synthesis of Supported Bimetallic Catalysts

## Overview

In this chapter, it is demonstrated that Rh or Pd nanoparticles can be decorated with reactive Fe atoms to form bimetallic RhFe or PdFe phase by controlled catalytic reduction of  $\text{Fe}_2\text{O}_3$  based support materials at a temperature lower than 250 °C. This can be achieved by first introducing ZnO additives to the  $\gamma\text{-Fe}_2\text{O}_3$  support at limited quantity. Upon calcination,  $\text{ZnFe}_2\text{O}_4$  is formed in excess of  $\text{Fe}_2\text{O}_3$  at a close proximity. Thus, a hetero-junction of  $\text{ZnFe}_2\text{O}_4\text{-Fe}_2\text{O}_3$  with staggered energy levels can be established, which then extends the lifetime of excitons. It is evident that thermal excited holes (as activated oxygen) accumulated in valence bands are allowed to react with the atomic H produced on the noble metal to form water before their recombination. Meanwhile, the corresponding excited electrons can promote the reduction of Fe(III) to Fe(0) atoms at the  $\text{ZnFe}_2\text{O}_4\text{-Fe}_2\text{O}_3$  hetero-junction interface. (Scheme 4-2) The amount of produced Fe(0) is governed by  $\text{ZnFe}_2\text{O}_4 : \text{Fe}_2\text{O}_3$  ratio in the support. As a result, a series of supported PdFe and RhFe bimetallic clusters with controllable compositions can be obtained with constant noble metal loading. The concept of hetero-junction is well-known in micro-electronics and solar cells (in multilayer thin film with much larger dimension), but tailoring the heterojunction interfaces in nano-size regime in support materials to prepare extremely reactive bimetallic catalysts has not been explored before this work.

## 4.1 Introduction

Metal nanoparticles supported on high surface area oxides are widely used as catalysts in many important industrial reactions.[1] But the choices of metal, oxide support, additive and their pretreatment conditions are generally formulated empirically from extensive screening of catalyst components. It has been demonstrated that many heterogeneous catalytic reactions require a specific metal and support interaction generally described as strong metal support interaction (SMSI) to give a high catalytic performance. [2] However, the precise modification of catalytic properties of the metal NPs by the support materials is not fully understood and could be complex in nature. It is becoming clear that one of the important causes for SMSI is the decoration of supported metal particles with trace reactive metallic elements derived from the support as bimetallic species. For example, much debate exists on the nature of active site of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst for methanol production from synthesis gas, despite more than 40 years intense research on this industrial catalyst. Recent research using advanced and sensitive instruments has shown that a very small quantity of Zn atoms is formed on Cu nanoparticles. This Zn decoration is believed to alter the electronic and thus the adsorptive properties of the Cu dramatically.[3,4] Similarly, Pd nanoparticles modified with Zn or Ga atoms, formed from Pd/ZnO or Ga<sub>2</sub>O<sub>3</sub> catalyst under reducing conditions, are shown to give superior activity and selectivity in a number of reforming reactions.[5,6]

On the other hand, the enhancement of catalytic properties by bimetallic nanoparticles dependent on composition prepared by a range of preparative techniques have been previously realized.[7,8] Theoretical calculations to appreciate the electronic modification of metallic surface by a secondary element have also been well studied.[9,10] However, the underlying principle for the *controlled modification* of supported metal nanostructure by the reactive metal atoms derived

from the reduction of the underneath metal oxide support in a specific catalytic reaction is not known. It is thus important to elucidate the mechanism for the reduction of refractory metal oxide supports and their effect in catalysis. In fact, there is intense interest in controlling the reduction process of the nano-region support materials with assistance of noble metal clusters. This will provide a new method for producing extremely small supported bimetallic particles with controllable composition at a specific interface without the use of reactive organic precursors or stabilizer(s) for catalytic, electrocatalytic (fuel cells) and sensor applications.

## **4.2 Synthesis of the materials**

Rhodium and palladium supported on iron oxide catalysts are taken as the examples to demonstrate the preparation of extremely small RhFe or PdFe bimetallic NPs through the controllable reduction of iron oxide support in presence of noble metal. Briefly, Zn(II) was blended into the precipitation process of Fe(III) to form a mixed oxides support, after which the noble metal (Pd(II) or Rh(III)) was loaded. The detailed synthesis procedure of a series of Rh<sub>2</sub>O<sub>3</sub>/ Fe<sub>2</sub>O<sub>3</sub> and PdO/ Fe<sub>2</sub>O<sub>3</sub> samples with variable Zn content was described in Chapter 3. The supported RhFe and PdFe bimetallic NPs are produced after pre-reduction of the samples.

## **4.3 Characterization of the Zn blended Fe<sub>2</sub>O<sub>3</sub> support (before reduction)**

### **4.3.1 Synchrotron X-ray Diffraction (SXRD) and Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES)**

Zn(II) was added to modify the structure of the primary Fe<sub>2</sub>O<sub>3</sub> support and the Zn concentration

was determined by ICP-AES as shown in Table 4-1. The SXRD patterns of samples 1-4 are shown in Figure 4-1; all samples can be indexed and identified to the spinel structure (space group:  $Fd-3m$ ). It is well known that  $\gamma\text{-Fe}_2\text{O}_3$  has a typical spinel structure in which  $\text{O}^{2-}$  are cubic closed packed while the Fe(III) occupy 1/8 tetrahedral sites and 1/2 octahedral sites. [11] When Zn(II) is blended to the system, some Fe(III) at the tetrahedral sites will be replaced, while the spinel structure is maintained. From empirical calculation, when all the Fe(III) at the tetrahedral sites are substituted by Zn(II), a stable  $\text{ZnFe}_2\text{O}_4$  phase can be formed, at which the concentration of zinc is 21.2 wt%. [12] Beyond this value, the ZnO phase will be formed. As shown in Table 4-1, the concentrations of zinc determined by ICP-AES in the samples are below this value. Consistent with this there is no diffraction peak of ZnO observed in SXRD. And the samples are composed of a mixture of  $\text{ZnFe}_2\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$  with the same lattice structure. The calculated ratio of  $\text{ZnFe}_2\text{O}_4$ :  $\text{Fe}_2\text{O}_3$  from the results of ICP-AES are also displayed in Table 4-1. Because of the strong overlap of the diffraction patterns, no differentiation of  $\text{Fe}_2\text{O}_3$  and  $\text{ZnFe}_2\text{O}_4$  is observed.

**Table 4-1** The compositions of a series zinc modified  $\text{Fe}_2\text{O}_3$  supports before the pre-reduction (the weight % of Zn was measured by ICP-AES).

| Sample | Mass of added<br>$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (g) | Mass of added<br>$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (g) | Weight %<br>of Zn | $\text{ZnFe}_2\text{O}_4$ : $\text{Fe}_2\text{O}_3$<br>(mole ratio) |
|--------|---------------------------------------------------------------------------|---------------------------------------------------------------------------|-------------------|---------------------------------------------------------------------|
| 1      | 0.00                                                                      | 10.41                                                                     | 0.00              | 0.0                                                                 |
| 2      | 1.18                                                                      | 7.90                                                                      | 11.8              | 0.6                                                                 |
| 3      | 1.48                                                                      | 7.50                                                                      | 13.5              | 1.0                                                                 |
| 4      | 2.29                                                                      | 6.40                                                                      | 20.8              | 8.6                                                                 |

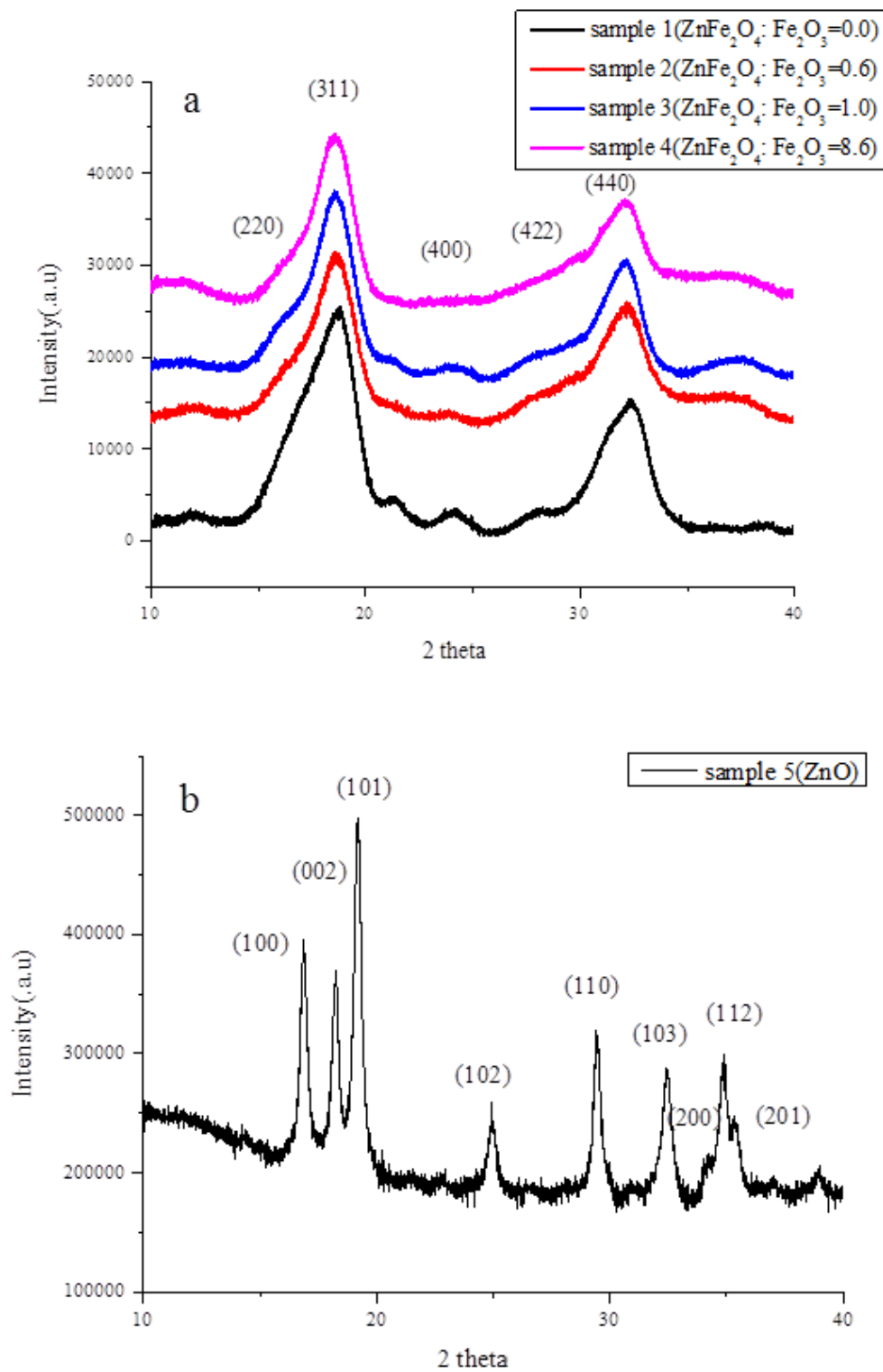


**Figure 4-1** SXRD patterns of ZnFe<sub>2</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> samples of various ratios: (a) samples 1-4 and (b) sample 5 (ZnO).

#### 4.3.2 Electron Energy Loss Spectroscopy (EELS) mapping

EELS mapping (Figure 4-2) was conducted to differentiate the two nano-sized  $\text{ZnFe}_2\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$  particles in samples 2-4 with variable R values (R is defined as the mole ratio of  $\text{ZnFe}_2\text{O}_4$ :  $\gamma\text{-Fe}_2\text{O}_3$ ). In all the samples, the distribution of oxygen is uniform. However, on the zinc mapping diagrams of samples 2 and 3, small black holes indicating weak or total absence of zinc signal are observed which should be assigned to the  $\text{Fe}_2\text{O}_3$  rich areas. The adjacent brighter area corresponds to the  $\text{ZnFe}_2\text{O}_4$  rich areas with relatively higher zinc concentration. Therefore, the co-existence of the two separate solid phases is confirmed by the uneven distribution of zinc element in the samples. In order to quantify the interface of these two phases, differentiation of the EELS digitalized signal ratios of iron to zinc scanning across the powder for samples 2-4 are displayed in Figure 4-2 (right). The observed peaks are the results of the drop in zinc concentration from the  $\text{ZnFe}_2\text{O}_4$  rich region with a constant Fe/Zn ratio to the main  $\text{Fe}_2\text{O}_3$  phase. Thus, a higher peak frequency in the scanned regions represents a larger quantity of  $\text{ZnFe}_2\text{O}_4$ - $\text{Fe}_2\text{O}_3$  interfaces. From the result, the peak frequency is the lowest in sample 4 where almost pure  $\text{ZnFe}_2\text{O}_4$  phase was made (calculated  $R=8.6$ ). In contrast, the sample 3 gives more peaks than the other samples with calculated R ratio of 1.0 that is characterized with the largest amount of interfaces.

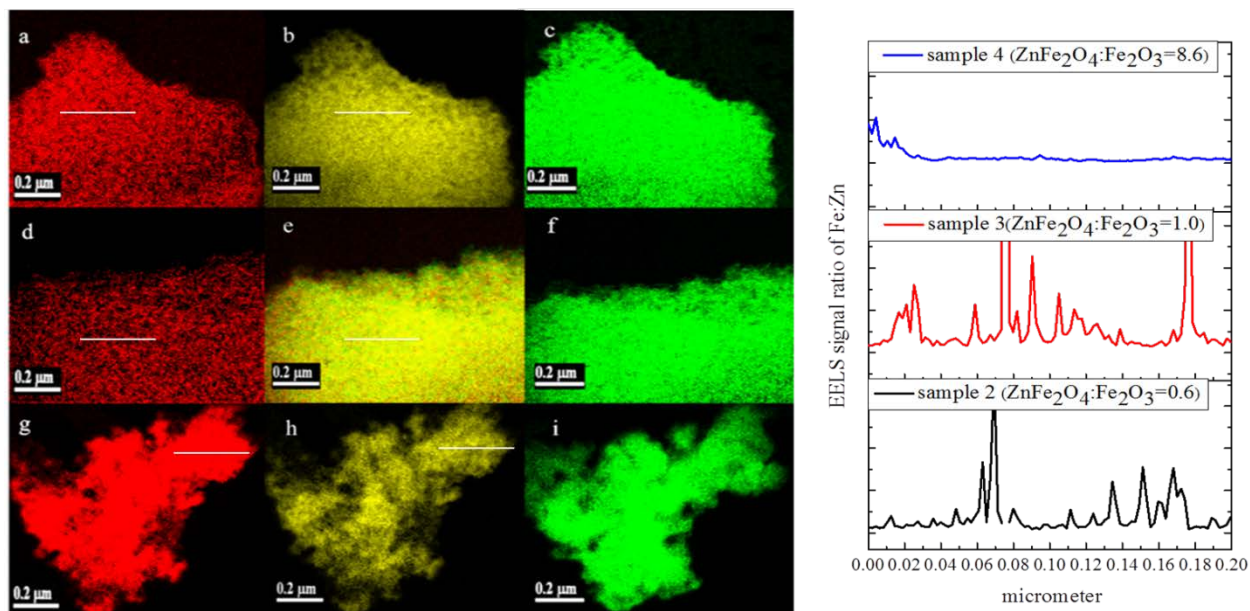


**Figure 4-2** Left: EELS mappings of zinc (red), iron (yellow) and oxygen (green) for sample 2 (a, b, c), sample 3 (d, e, f) and sample 4 (g, h, i); Right: Differential EELS digital signal ratios of Fe:Zn scanned across the powder for sample 2 ( $R=0.6$ ), sample 3 ( $R=1.0$ ), and sample 4 ( $R=8.6$ ) (the white lines indicate the area of EELS digitalization).

With the combined results of SXRD, ICP-AES and EELS mapping, it is concluded that the zinc blended iron oxide support is composed of  $\gamma$ - $\text{Fe}_2\text{O}_3$  and  $\text{ZnFe}_2\text{O}_4$  with variable mole ratio. And the concentration of  $\text{ZnFe}_2\text{O}_4$ - $\text{Fe}_2\text{O}_3$  interface among the samples orders as sample 3 ( $R=1.0$ ) > sample 2 ( $R=0.6$ ) > sample 4 ( $R=8.6$ ) > sample 1 ( $R=0.0$ ).

## 4.4 Characterization of supported RhFe bimetallic NPs (after reduction)

With a loading of 5 wt% Rh, the composition of the active metal phase is thoroughly investigated.

### 4.4.1 Temperature Programmed Reduction (TPR)

TPR was used to investigate the reduction behavior of catalysts and estimate the amounts of Fe metal atoms produced after the reduction. The TPR curves of a series Rh<sub>2</sub>O<sub>3</sub>/ZnFe<sub>2</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> samples with variable composition are displayed in Figure 4-3. The total H<sub>2</sub> consumption from the curve integration is labelled in the figure. According to the stoichiometric equations:



0.8 mmol and 2.0 mmol H<sub>2</sub> per gram catalyst are needed to reduce the Rh<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> in sample 1 into metallic Rh and Fe<sub>3</sub>O<sub>4</sub>, respectively. It is noted that the H<sub>2</sub> consumption value for Rh<sub>2</sub>O<sub>3</sub>/Fe<sub>2</sub>O<sub>3</sub> (sample 1, 3.2 mmol (g cat)<sup>-1</sup>, cat is abbreviation of catalyst) is slightly higher than the sum of theoretical values for the two processes of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> (2.0 mmol (g cat)<sup>-1</sup>) and Rh<sub>2</sub>O<sub>3</sub> to Rh(0) (0.8 mmol (g cat)<sup>-1</sup>). This implies Rh<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> have been reduced to Rh(0) and Fe<sub>3</sub>O<sub>4</sub> respectively. A small quantity of Fe(0) is also produced through the further reduction of Fe<sub>3</sub>O<sub>4</sub> (in contact with Rh). The amount of extra H<sub>2</sub> consumption beyond the stoichiometric value of Rh<sub>2</sub>O<sub>3</sub> to Rh(0) plus Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> varies with the ratios of ZnFe<sub>2</sub>O<sub>4</sub>:Fe<sub>2</sub>O<sub>3</sub>. This suggests the formation of Fe(0) of various quantities (shown in Table 4-2): sample 1 (R=0.0) < sample 4 (R=8.6) < sample 2 (R=0.6) < sample 3 (R=1.0). Zn(II) will not be reduced in the presence of Fe(II) due to the much more negative reduction potential of Zn(II) to Zn(0) than that of Fe(II) to Fe(0) (E<sub>0</sub>[Zn(II)/Zn(0)] = -0.76 V, E<sub>0</sub>[Fe(II)/Fe(0)] = -0.44 V).

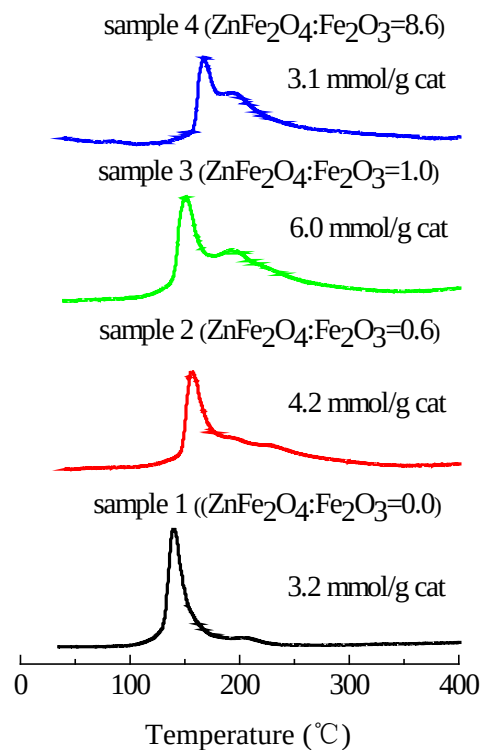


**Figure 4-3** TPR curves for a series of Rh<sub>2</sub>O<sub>3</sub>/ ZnFe<sub>2</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> samples.

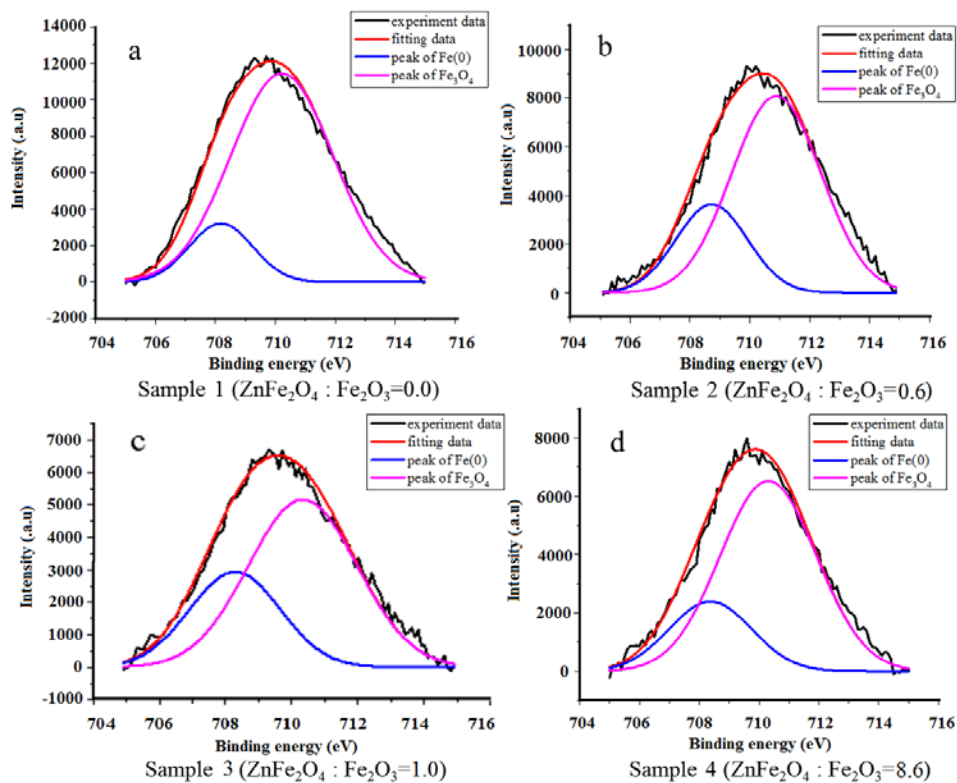
**Table 4-2** The calculated amount of produced Fe(0) from TPR for Rh<sub>2</sub>O<sub>3</sub>/ZnFe<sub>2</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> samples.

|                                                            | Sample 1<br>(R=0.0) | Sample 2<br>(R=0.6) | Sample 3<br>(R=1.0) | Sample 4<br>(R=8.6) |
|------------------------------------------------------------|---------------------|---------------------|---------------------|---------------------|
| <b>Produce Fe(0)</b><br><b>(mmol (g cat)<sup>-1</sup>)</b> | 0.34                | 1.34                | 2.76                | 0.75                |

#### 4.4.2 X-ray Photoelectron Spectroscopy (XPS)

The XPS curves of Fe and Rh in a series of reduced Rh/ZnFe<sub>2</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> samples are shown in Figure 4-4 and Figure 4-5, respectively. For Fe, all the curves can be fitted by two peaks located

at around 708 eV and 711 eV, respectively. As previously reported, the former one is assigned to the signal of Fe(0) while the other one with higher binding energy corresponds to the signal of the Fe<sub>3</sub>O<sub>4</sub>.<sup>[13,14]</sup> It is noted that the ratio of the two peaks (signal of Fe(0)/Fe<sub>3</sub>O<sub>4</sub>) varies with the composition of the samples. As shown in Table 4-3, the value orders as sample 1 (R=0.0) < sample 4 (R=8.6) < sample 2 (R=0.6) < sample 3 (R=1.0) indicating the increasing content of Fe(0) among samples. This is in agreement with the results of TPR. For Rh 3d XPS, the binding energy of Rh 3d is progressively attenuated with increasing amount of Fe(0), which reaches a minimum at sample 3 (R=1.0). This can be accounted for by the fact that Fe is more prone to lose its electrons to Rh in their shared electronic bands (electronegativity of 1.8 and 2.3 for Fe and Rh atom respectively, electronegativity is defined as a measure of the ability of a specified atom to attract electrons in lattice structure or in a molecule) indicating the strong interaction of Fe and Pd atoms in proximity.



|          | Whole FWHM<br>(eV) | FWHM for Fe(0)<br>(eV) | FWHM for Fe <sub>3</sub> O <sub>4</sub><br>(eV) |
|----------|--------------------|------------------------|-------------------------------------------------|
| Sample 1 | 4.9                | 2.4                    | 3.9                                             |
| Sample 2 | 4.7                | 2.8                    | 3.8                                             |
| Sample 3 | 4.5                | 3.0                    | 3.7                                             |
| Sample 4 | 4.6                | 3.2                    | 3.8                                             |

**Figure 4-4** (Top) XPS curves of Fe 2p<sub>3/2</sub> in a series of reduced Rh/ZnFe<sub>2</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> samples; (Bottom) the FWHM (Full width at half maximum) values for the whole Fe XPS curves (whole FWHM), the fitted Fe(0) peaks and the fitted Fe<sub>3</sub>O<sub>4</sub> peaks, respectively.

**Table 4-3** The ratio of Fe signal in metallic Fe(0) and Fe<sub>3</sub>O<sub>4</sub> for the reduced Rh samples.

| Sample       | Signal ratio of Fe(0): Fe <sub>3</sub> O <sub>4</sub> |
|--------------|-------------------------------------------------------|
| 1<br>(R=0.0) | 0.18                                                  |
| 2<br>(R=0.6) | 0.41                                                  |
| 3<br>(R=1.0) | 0.48                                                  |
| 4<br>(R=8.6) | 0.31                                                  |

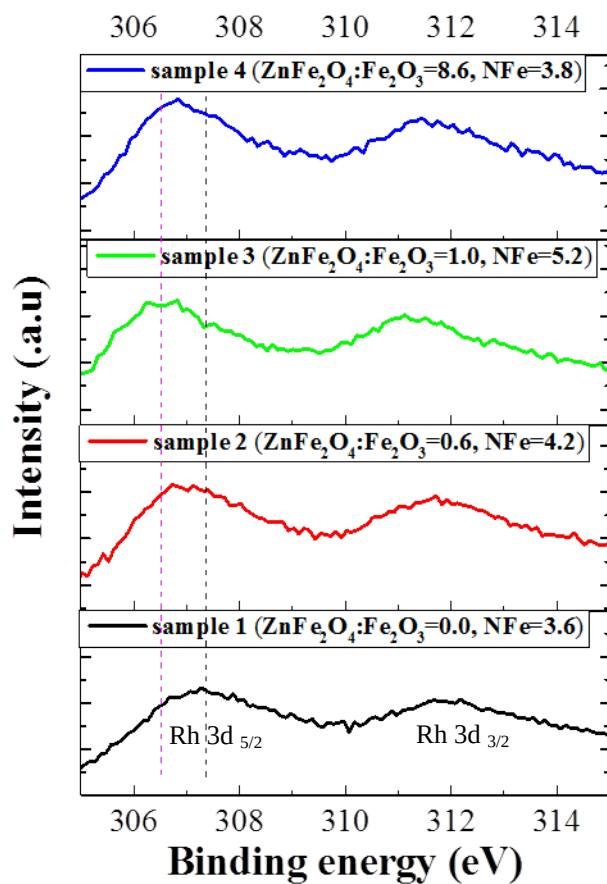


**Figure 4-5** Rh 3d XPS curves for sample 1-4 after pre-reduction.

#### 4.4.3 Extended X-ray Absorption Fine Structure (EXAFS)

Assuming that noble metal is the active site for producing atomic H and assists catalytic reduction of the iron oxide support to metallic Fe(0), the produced Fe atoms will decorate or react with noble metal NPs at close proximity to form bimetallic clusters. The EXAFS at Rh K edge is thus employed to reveal the interaction between Rh and Fe atoms. The results for a series of reduced Rh samples are shown in Figure 4-6 and Table 4-4. It is noted the total coordination number (CN) of Rh for all samples are in a range from 6.4 to 7.1. These low values suggest that the produced metallic Rh containing phase is still maintained at extremely small size despite the fact that the progressive addition of Zn(II) appears to increase the metallic size slightly. We have estimated the average size of the nanoparticles to be around 1.5 nm based on a recent Rh EXAFS study alongside other techniques (gas adsorption, TEM and FTIR). [15] The most striking feature in EXAFS is the observation of a shorter scattering path of 2.55 Å compared with a typical 2.67 Å Rh-Rh scattering path in nano-sized Rh particles (Figure 4-6b).[15] This is assigned to the first shell scattering pair of Rh-Fe. Sample 3 (R=1.0) gives the highest number of first shell neighbour Fe to Rh (NFe=5.2) followed by sample 2 (NFe=4.2) > sample 4 (NFe=3.8) > sample 1 (NFe=3.6). The result reflects the various composition of RhFe nanoparticles as shown in Figure 4-6a (dependent on Zn ions added). Figure 4-7 displays the experimental and fitting curves of the Rh EXAFS in  $k^3$  space.

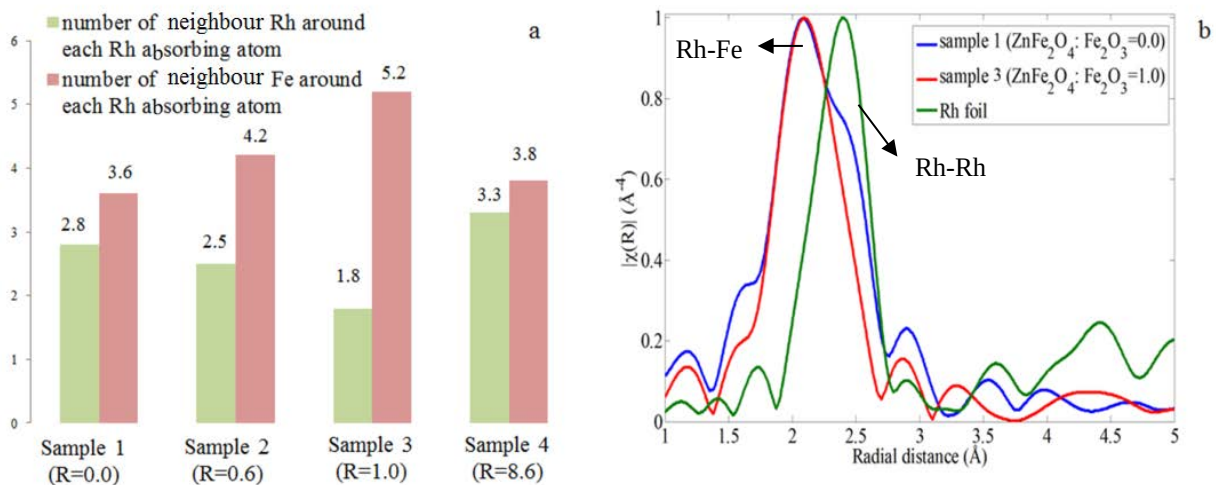
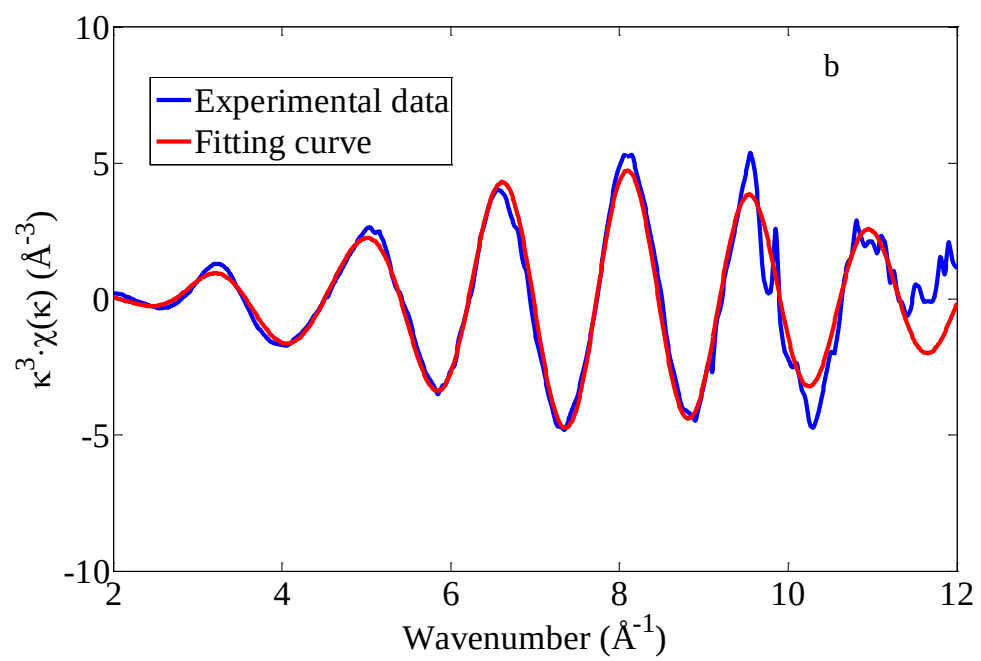
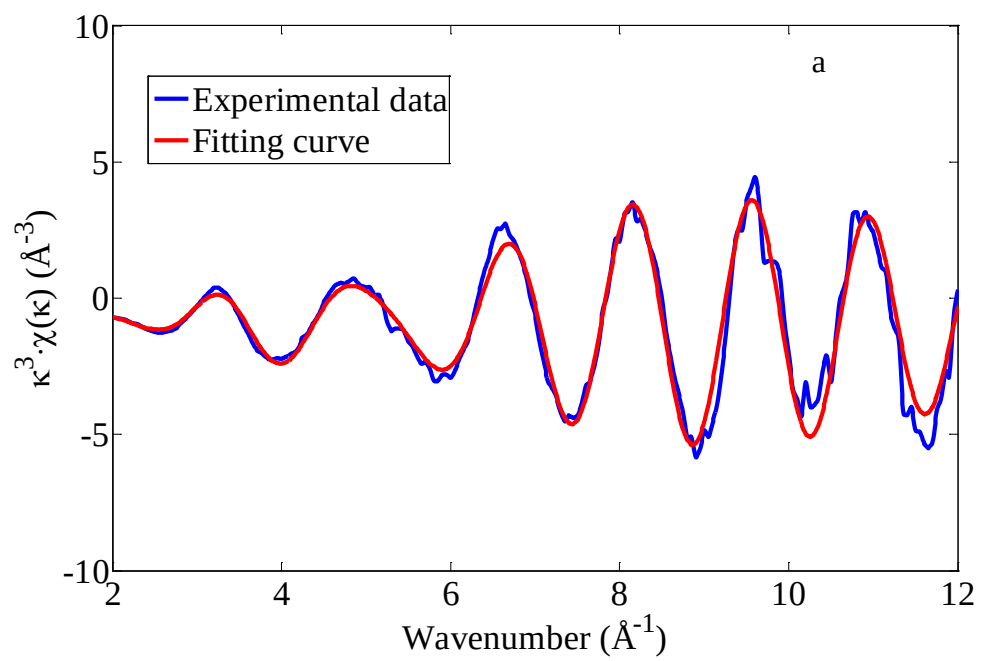


**Figure 4-6** (a) Number of neighbour Rh (NRh) and Fe (NFe) atoms around Rh absorbing atom derived from EXAFS fittings; (b) The typical EXAFS curves against radial distance for sample 1 (R=0.0) and sample 3 (R=1.0) with a reference of Rh foil.

**Table 4-4** Average coordination environment of Rh atom derived from EXAFS results for a series of reduced Rh/ZnFe<sub>2</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> samples.

| Sample | Total CN | $\Delta E$ (eV) | Rh-Rh distance (Å) | D-W factor (Å <sup>2</sup> ) | Rh-Fe distance (Å) | D-W factor (Å <sup>2</sup> ) | R-factor |
|--------|----------|-----------------|--------------------|------------------------------|--------------------|------------------------------|----------|
| 1      | 6.4(6)   | -3.0            | 2.67(1)            | 0.005(1)                     | 2.56(1)            | 0.010(2)                     | 2.9%     |
| 2      | 6.7(6)   | -5.0            | 2.66(1)            | 0.011(2)                     | 2.54(1)            | 0.008(1)                     | 1.6%     |
| 3      | 7.0(3)   | -5.0            | 2.67(1).           | 0.006(1)                     | 2.54(1)            | 0.010(1)                     | 0.7%     |
| 4      | 7.1(6)   | -1.0            | 2.65(1)            | 0.010(1)                     | 2.55(1)            | 0.013(1)                     | 2.8%     |

("CN" is coordination number; " $\Delta E$ " is the energy difference between the experimental absorption energy and the calculated value in curve fitting; "D-W" is Debye Waller; "R factor" is the indication of the quality of curve fitting)



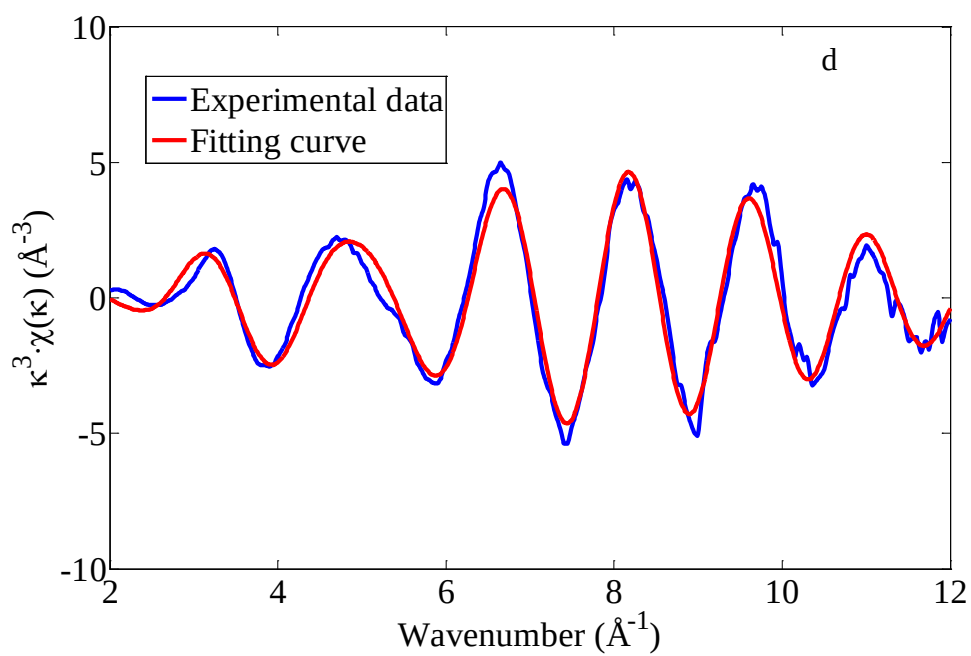
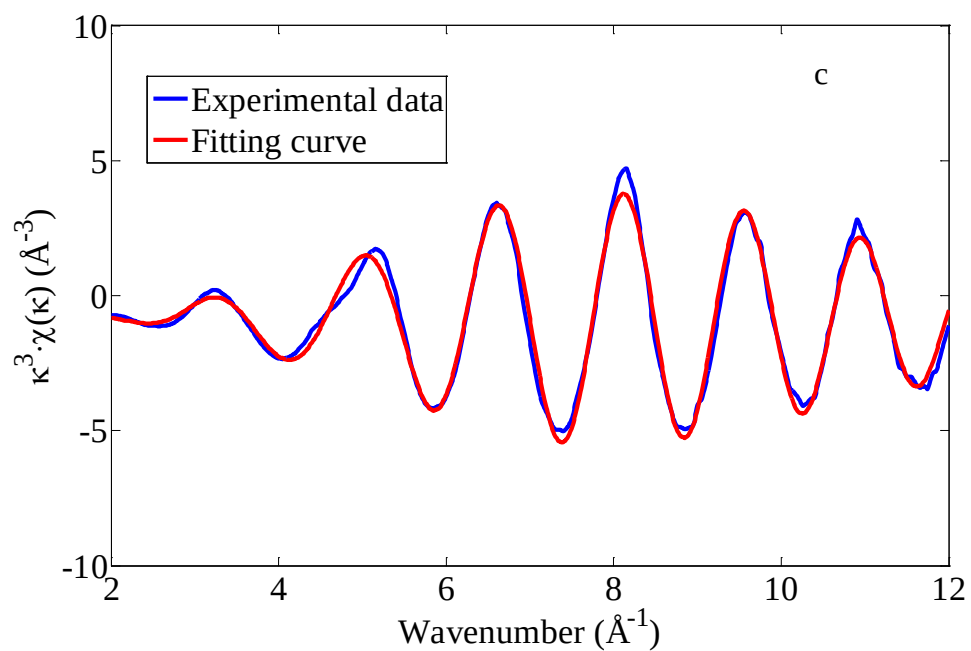


**Figure 4-7**  $k^3$  space EXAFS curves of Rh in (a) sample 1 (R = 0.0), (b) sample 2 (R = 0.6), (c) sample 3 (R = 1.0), (d) sample 4 (R = 8.6). (blue: experiment data; red: fitting data)

#### 4.4.4 Transmission Electron Microscopy (TEM)

Figure 4-8 displays the TEM images of reduced Rh samples with various ratios of  $\text{ZnFe}_2\text{O}_4\text{:Fe}_2\text{O}_3$  in the supports and their corresponding particle size distribution. The average size of noble metal particles is around 1-2 nm, almost the same for both samples. The results are consistent with the estimation from EXAFS.

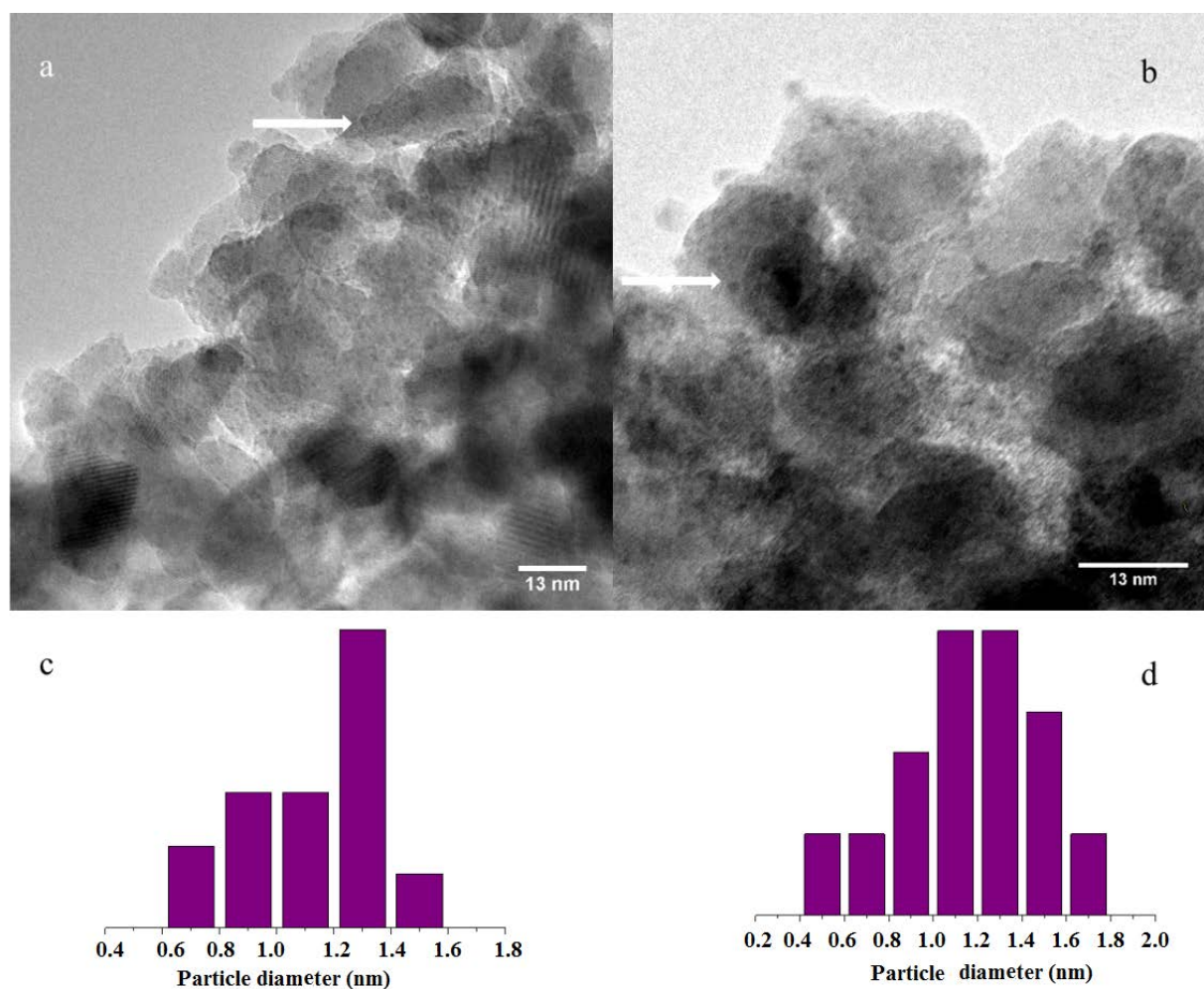


**Figure 4-8** TEM images of reduced Rh samples (a) reduced sample 1 ( $R = 0.0$ ) and (b) reduced sample 3 ( $R = 1.0$ ); (c) the Rh particle size distribution for sample 1 and (d) the Rh particle size distribution for sample 3.

## 4.5 Characterization of supported PdFe bimetallic NPs (after reduction)

The novel  $\text{ZnFe}_2\text{O}_4\text{-Fe}_2\text{O}_3$  support was also applied to the preparation of supported PdFe bimetallic NPs. With a loading of 5 wt% Pd, a series of  $\text{PdO/Fe}_2\text{O}_3\text{-ZnFe}_2\text{O}_4$  samples were synthesized. The TPR curves with labeled  $\text{H}_2$  consumption for the Pd samples are shown in Figure 4-9.

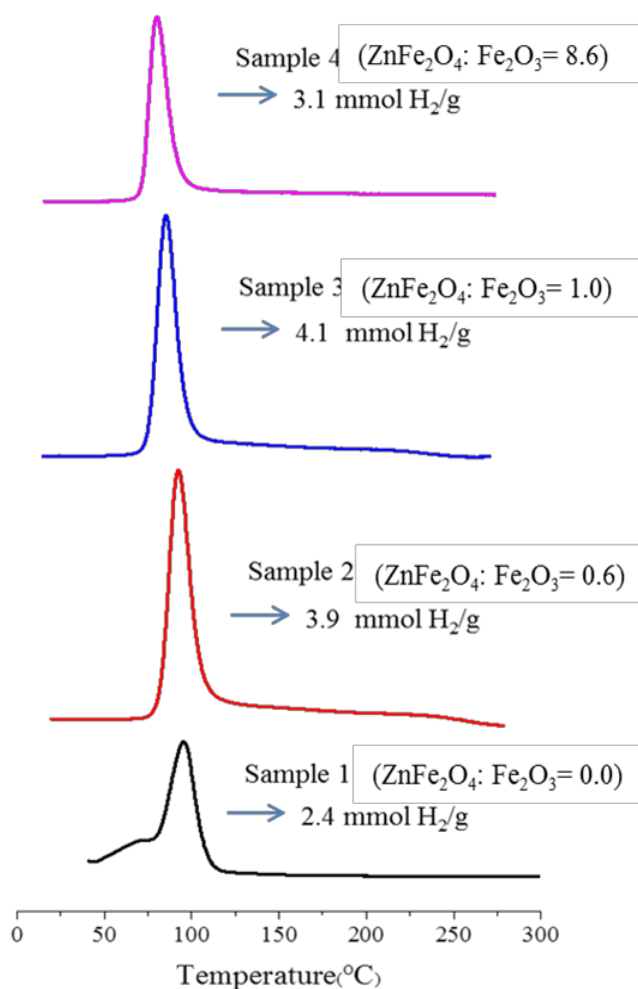


**Figure 4-9** TPR profiles for a series of  $\text{PdO/ZnFe}_2\text{O}_4\text{-Fe}_2\text{O}_3$  samples.

It is well accepted the reduction of  $\text{PdO} \rightarrow \text{Pd}$  happens at sub-ambient temperature. Thus the peaks in TPR profiles are attributed to the reduction process of  $\text{Fe}_2\text{O}_3$ . For sample 1 ( $R=0.0$ ) without the effect of blended  $\text{Zn(II)}$ , the  $\text{H}_2$  consumption ( $2.4 \text{ mmol (g cat)}^{-1}$ ) is slightly higher than the theoretical value for transforming all  $\text{Fe}_2\text{O}_3$  into  $\text{Fe}_3\text{O}_4$  ( $2.0 \text{ mmol (g cat)}^{-1}$ ). This means all the  $\text{Fe}_2\text{O}_3$  in sample 1 can be reduced to  $\text{Fe}_3\text{O}_4$  completely and a small amount of  $\text{Fe(0)}$  is produced through the further reduction of  $\text{Fe}_3\text{O}_4$  with Pd in proximity. Similarly with the results of the Rh system, the extra  $\text{H}_2$  consumption beyond the process of  $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$  is also in the order of sample 1 ( $R=0.0$ ) < sample 4 ( $R=8.6$ ) < sample 2 ( $R=0.6$ ) < sample 3 ( $R=1.0$ ). The results allude to the production of variable amount of  $\text{Fe(0)}$  in these samples. The amounts of produced  $\text{Fe(0)}$  calculated from TPR for Pd series are shown in Table 4-5.

**Table 4-5** The calculated amounts of produced  $\text{Fe(0)}$  from TPR for a series of  $\text{PdO/ZnFe}_2\text{O}_4\text{-Fe}_2\text{O}_3$  samples.

|                                                                                      | Sample 1<br>( $R=0.0$ ) | Sample 2<br>( $R=0.6$ ) | Sample 3<br>( $R=1.0$ ) | Sample 4<br>( $R=8.6$ ) |
|--------------------------------------------------------------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| <b>Produce <math>\text{Fe(0)}</math><br/>(<math>\text{mmol (g cat)}^{-1}</math>)</b> | 0.23                    | 1.67                    | 1.97                    | 1.39                    |

With presence of Pd clusters in proximity, a series of supported PdFe bimetallic NPs with variable compositions at high dispersion were also synthesized. The corresponding XPS, EXAFS and TEM results are described in detail in Chapter 5

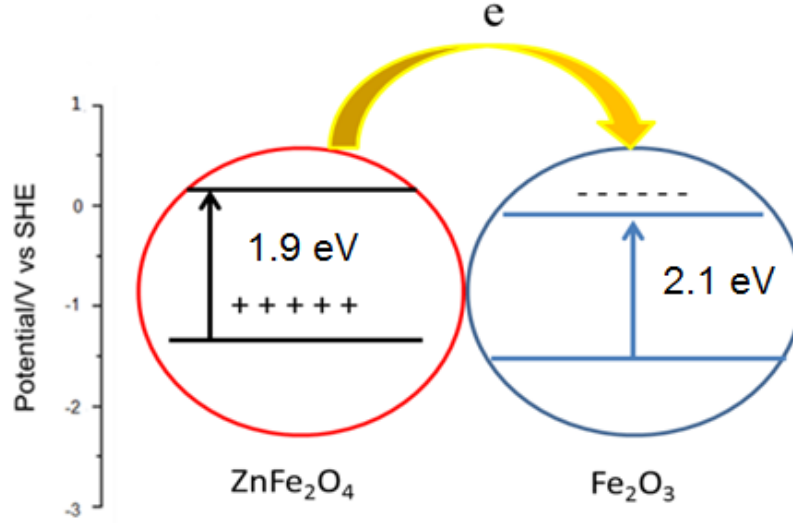
The combined characterization results confirm that the reduction of Fe ions (in the support) to metallic  $\text{Fe(0)}$  can be achieved at moderate temperature ( $< 250 \text{ }^\circ\text{C}$ ). The amount of  $\text{Fe(0)}$  formed can be tuned by blending of  $\text{Zn(II)}$  into iron oxide system through the formation of  $\text{ZnFe}_2\text{O}_4$  in

excess  $\text{Fe}_2\text{O}_3$ . In the presence of noble metal (Rh or Pd), a series of extremely small supported RhFe or PdFe bimetallic NPs with variable compositions can be prepared successfully without much particle size alteration.

## **4.6 Discussion of the reduction mechanism of $\text{ZnFe}_2\text{O}_4\text{-Fe}_2\text{O}_3$ support**

As shown by TPR, XPS and EXAFS, the content of Fe in the RhFe or PdFe bimetallic phase follows the order of sample 1 ( $R=0.0$ ) < sample 4 ( $R=8.6$ ) < sample 2 ( $R=0.6$ ) < sample 3 ( $R=1.0$ ). This increases with the amount of  $\text{ZnFe}_2\text{O}_4\text{-Fe}_2\text{O}_3$  interface (as shown by EELS) in the support.

With the co-existence of  $\text{ZnFe}_2\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  (as suggested in section 4.3), a type II hetero-junction can be established at the interface of the two phases with staggered energy levels. It is well accepted when two semi-conductors with staggered energy levels are placed in proximity, the alignment of their conduction and valence bands at the interface favours the separated location of the excitons as shown in Scheme 4-1.[16, 17, 18] The excited electrons reside in conduction band of  $\text{Fe}_2\text{O}_3$  whilst the holes in valence band of  $\text{ZnFe}_2\text{O}_4$ . Therefore, the recombination rate of electrons and holes is expected to decrease and their lifetime should be extended by the two materials.[19]



**Scheme 4-1** Exciton separation of type II hetero-junction with  $\text{ZnFe}_2\text{O}_4\text{-Fe}_2\text{O}_3$ .

To demonstrate the effect of spatial charge separation in this novel hetero-junction support, time resolved photoluminescence spectroscopy (TRPL) was employed. The recorded femtosecond (fs) PL spectra at time intervals and the kinetic decay profiles at 500-700 nm for sample 3 with the largest amount of hetero-junction interfaces ( $R=1.0$ ) is shown in Figure 4-10. Pure phases of  $\text{Fe}_2\text{O}_3$  and  $\text{ZnFe}_2\text{O}_4$  are used as the references without any hetero-junction effect. The lifetime parameters are derived from fitting the kinetic decay profiles with the multi-exponential function,

$$I = \sum_{i=1}^n A_i \exp\left(-\frac{t}{\tau_i}\right) \quad (\text{Equation 4-1})$$

where  $I$  is the normalized intensity,  $A$  is the associated amplitude parameter,  $t$  is the arrival time of detected emitted photon,  $\tau$  is the lifetime parameter. [20, 21] The results are summarized in Table 4-6. It is clear that the pure phases  $\text{Fe}_2\text{O}_3$  and  $\text{ZnFe}_2\text{O}_4$  showed relatively shorter lifetimes of excitons. The significantly longer lifetimes ( $\tau_3$  and  $\tau_4$ ) in sample 3 reaching nano-second regime can be attributed to the separation of excited electrons and holes across the hetero-

junction interface upon irradiation. Interestingly, the order of magnitude in these time constants is comparable to those of chemical reactions as reported in photocatalytic reactions. [22]

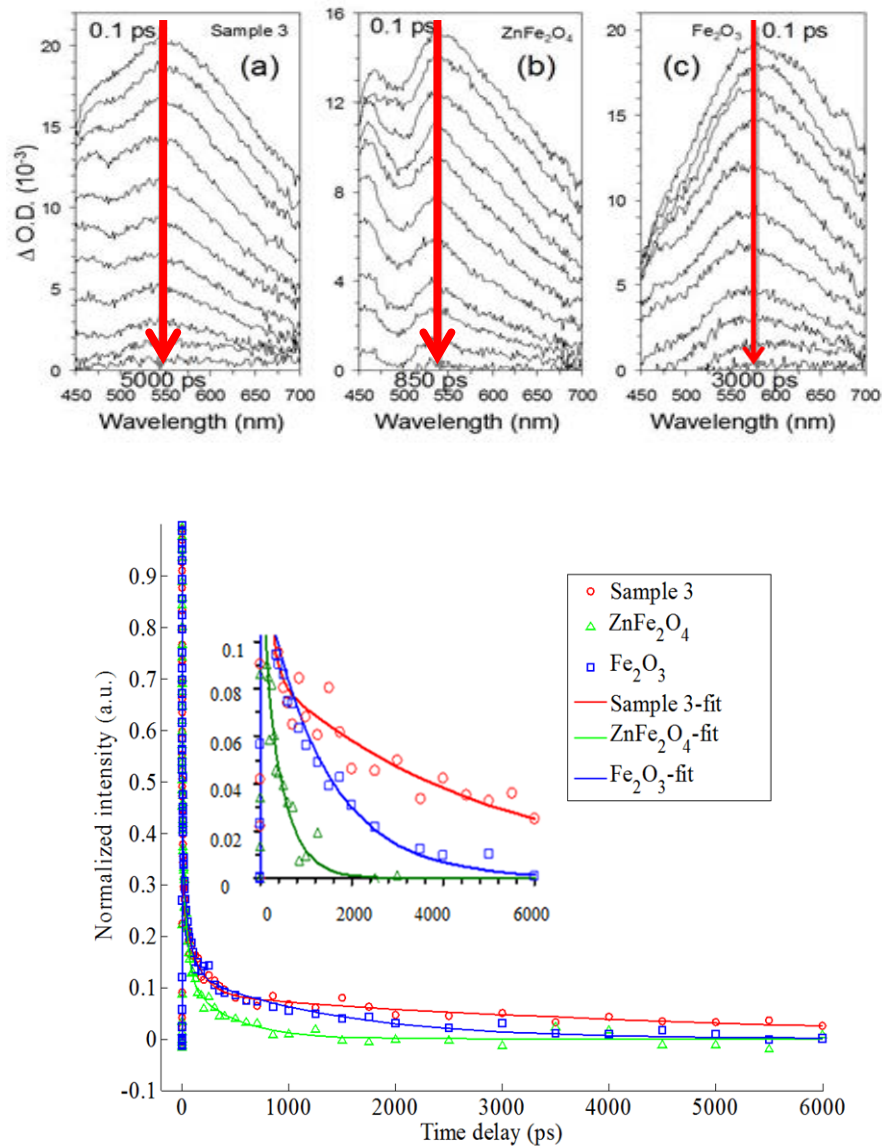


**Figure 4-10** (Top) fs photoluminescence spectra recorded for (a) sample 3 ( $R = 1.0$ ) at time intervals 0.1, 0.2, 0.35, 0.7, 1.75, 6, 15, 50, 250, 1500 and 5000 ps; (b)  $ZnFe_2O_4$  at time intervals 0.1, 0.2, 0.35, 0.7, 1.5, 5, 20, 50, 100, 200 and 850 ps; and (c)  $Fe_2O_3$  at time intervals 0.1, 0.25, 0.35, 0.6, 1.5, 6, 17.5, 60, 175, 850 and 3000 ps after excitation at 350 nm in water. (Bottom) Normalized experimental and fitted kinetic decay profiles of photoluminescence at 500-700 nm for sample 3 ( $\circ$ ),  $ZnFe_2O_4$  ( $\Delta$ ), and  $Fe_2O_3$  ( $\square$ ); the region of 0-0.1 normalized intensity is enlarged in the inserted figure.

**Table 4-6** Time constants ( $\tau$ ) and the associated amplitudes (a) of sample 3 (R = 1.0), Fe<sub>2</sub>O<sub>3</sub>, and ZnFe<sub>2</sub>O<sub>4</sub> measured by TRPL.

| Sample name                      | $t_{av} (t_{av} = \sum \tau_i \times a_i)$<br>(ps) | $\tau 1$ (ps)<br>(a1%) | $\tau 2$ (ps)<br>(a2%) | $\tau 3$ (ps)<br>(a3%) | $\tau 4$ (ps)<br>(a4%) |
|----------------------------------|----------------------------------------------------|------------------------|------------------------|------------------------|------------------------|
| ZnFe <sub>2</sub> O <sub>4</sub> | 52.80                                              | 0.47<br>(52)           | 4.74<br>(15)           | 41.36<br>(23)          | 423.35<br>(10)         |
| Fe <sub>2</sub> O <sub>3</sub>   | 160.94                                             | 0.49<br>(49)           | 7.15<br>(22)           | 64.24<br>(18)          | 1341.51<br>(11)        |
| sample 3<br>(R = 1.0)            | 353.64                                             | 0.43<br>(56)           | 8.99<br>(23)           | 135.41<br>(14)         | 4748.17<br>(7)         |

Electron paramagnetic resonance (EPR) (Figure 4-11a) and static photoluminescence (PL) (Figure 4-12) were employed to characterize the surface state of the supports with two distinctive phases. All the EPR spectra show a signal around  $g=1.96$  which reflects the existence of thermally excited but trapped unpaired electrons (separated electrons) on iron oxide surface. [23] The intensity of the signal varies with the composition of the supports: sample 1 (R=0.0) < sample 4 (R=8.6) < sample 2 (R=0.6) < sample 3 (R=1.0), which follows the order of increasing amount of ZnFe<sub>2</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> interfaces indicated by EELS. Indeed, the ZnFe<sub>2</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> heterojunction can stabilize the excitons by the spatial separation of electrons and holes. Thus, some thermally excited electrons accumulating on the surface of iron oxide with a prolonged lifetime are observed by EPR before they recombine with the holes on ZnFe<sub>2</sub>O<sub>4</sub> rich region. Therefore, the EPR signal reaches the highest value at sample 3 (R=1.0) with the highest concentration of ZnFe<sub>2</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> interface. The spin number reaches  $1.9 \times 10^{20} \text{ g}^{-1}$ .

The PL spectra of samples 1-4 are displayed in Figure 4-12; two peaks are observed in all the samples after a careful peak fitting at around 500 nm and 600 nm, respectively. The former is due to the characteristic exciton recombination of nano-sized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (I<sub>i</sub>). And the latter with longer emission wavelength (I<sub>g</sub>) is due to the presence of neutral or singularly charged oxygen species (thermally activated holes) in the structure as electron trapped sites.[24] The ratio between the integration area of the two peaks in terms of I<sub>g</sub>/I<sub>i</sub> varies among the samples as shown in Table 4-7. The result exhibits the same trend as shown by the EPR result: sample 1 (R = 0.0) < sample 4 (R = 8.6) < sample 2 (R = 0.6) < sample 3 (R = 1.0). Once again sample 3 with the highest content of hetero-junction interface gives the largest value which suggests the highest concentration of active oxygen species (thermally activated holes) in this sample.

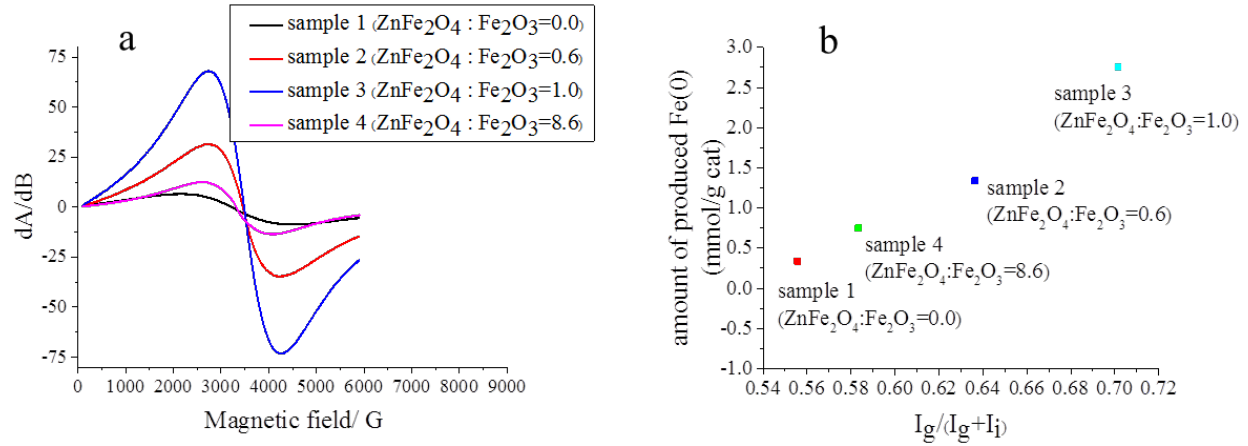


**Figure 4-11** (a) EPR spectra of samples 1-4. (b) The relationship between the I<sub>g</sub>/(I<sub>g</sub>+I<sub>i</sub>) from the static PL spectra and the amount of produced Fe(0) calculated from the TPR results for sample 1-4. (I<sub>g</sub> and I<sub>i</sub> refer to the integration area of the peaks of long emission (600 nm) and instant recombination (500 nm) of the oxide supports in PL spectra, as shown in Figure 4-12).

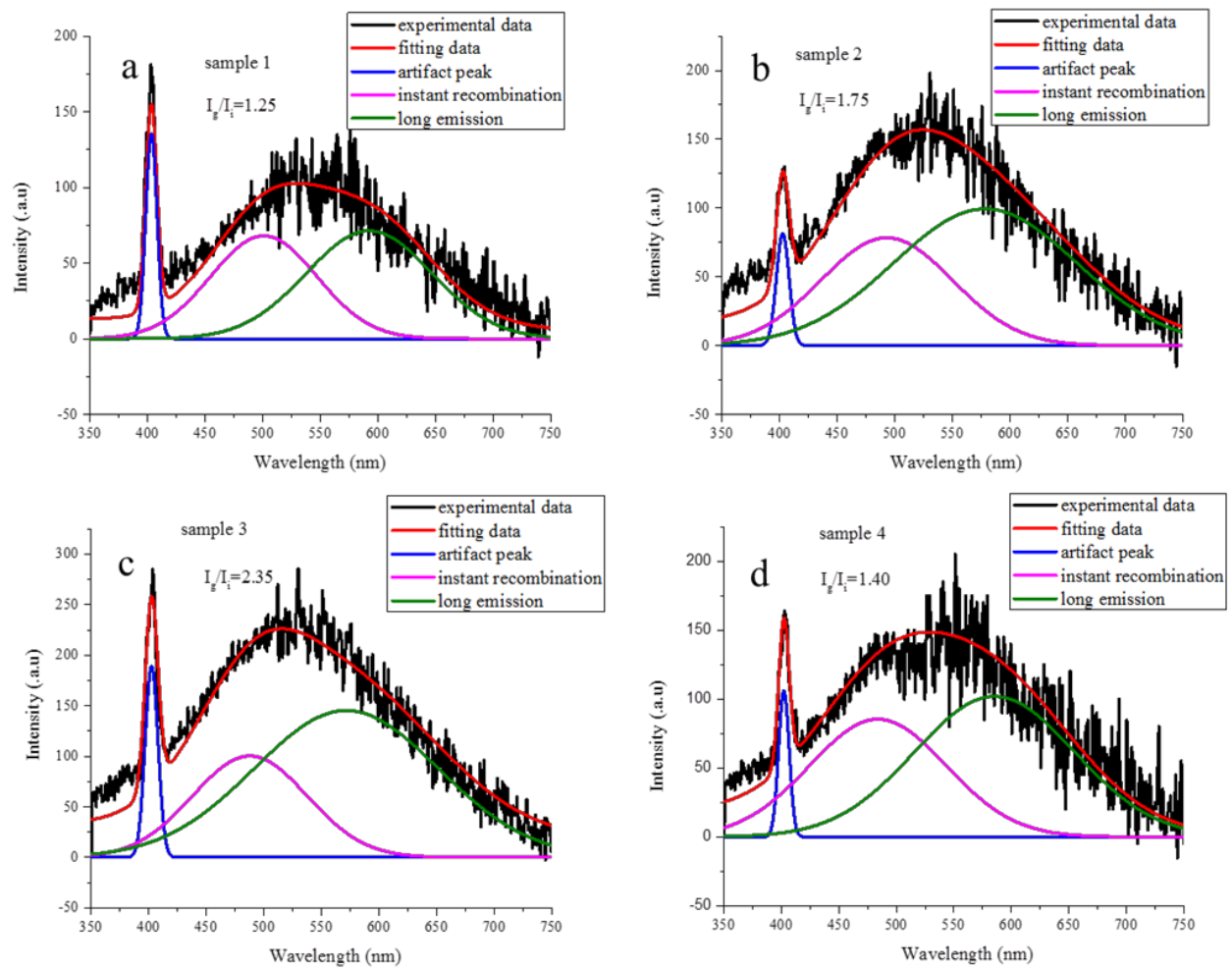


**Figure 4-12** The static photoluminescence (PL) spectra for (a) sample 1 ( $R=0.0$ ); (b) sample 2 ( $R=0.6$ ); (c) sample 3 ( $R=1.0$ ); (d) sample 4 ( $R=8.6$ ). (The peak located at 400 nm is assigned to an artifact peak due to the instrument.)

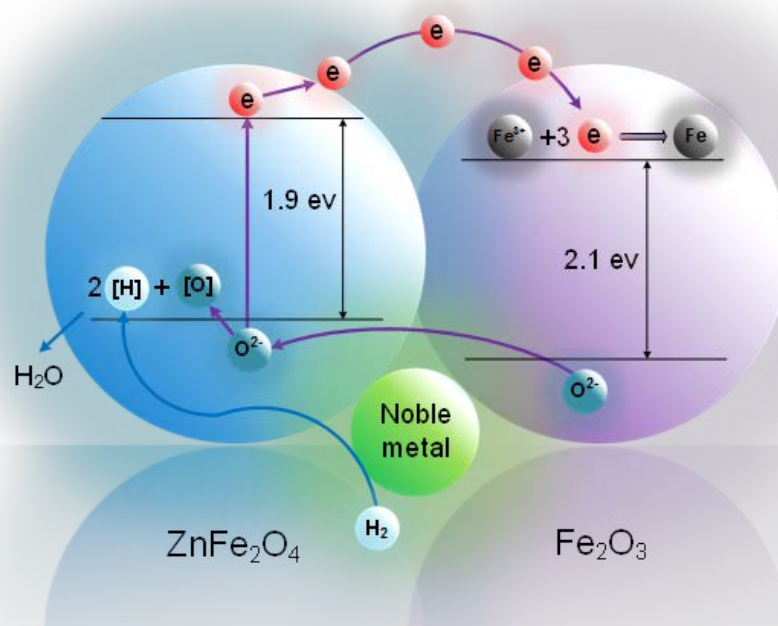
**Table 4-7** The value of  $I_g/I_i$  in PL spectra for samples 1-4 with variable  $R$  ratios.

| Sample    | 1<br>( $R=0.0$ ) | 2<br>( $R=0.6$ ) | 3<br>( $R=1.0$ ) | 4<br>( $R=8.6$ ) |
|-----------|------------------|------------------|------------------|------------------|
| $I_g/I_i$ | 1.25             | 1.75             | 2.35             | 1.40             |

In a typical semi-conductor oxide, some thermal- or photo- ‘excited electrons’ can momentarily overcome the forbidden band gap and occupy the higher energy conduction band which is primarily composed of empty bands of cations. The corresponding ‘holes’ will take residence in the lower energy valence band that is constituted mainly by occupied  $2p$  band of oxygen ions. Thus, the term ‘hole’ in a semiconductor oxide can be appreciated chemically as activated oxygen species with lower formal charge (neutral or singularly charged oxygen) than lattice oxygen ions. However, the majority of the excited electrons and holes (excitons) will recombine rapidly in the single phase semiconductor oxide support with short lifetime (i.e.  $\text{Fe}_2\text{O}_3$  or  $\text{ZnFe}_2\text{O}_4$  only) as reflected by the TRPL data. On the other hand, we have shown that the establishment of  $\text{ZnFe}_2\text{O}_4\text{-Fe}_2\text{O}_3$  type II hetero-junction can greatly prolong the lifetime of excitons in the two-phase support. With the extension of exciton lifetime, more and more activated oxygen species are accumulated on the surface, particularly in sample 3 as indicated by the PL spectra. When noble metal is in proximity, these activated oxygen species (holes) can react with the spilled atomic hydrogen (produced on noble metal surface) to form water as their lifetime constant is comparable to that of this chemical reaction. Meanwhile, the corresponding excited electrons will reduce Fe(III) in the support to form metal atoms. Indeed, PL and TPR results have demonstrated that the amount of Fe(0) formed in TPR is correlated to the amount of active oxygen species (holes) produced. The amount of produced Fe(0) gives a linear relationship with respect to  $I_g/(I_g+I_i)$  (Fig 4-11(b)). Therefore, the reduction of Fe(III) into Fe(0) is significantly facilitated by the  $\text{ZnFe}_2\text{O}_4\text{-Fe}_2\text{O}_3$  hetero-junction interface.

Sample 3 ( $R=1.0$ ) produces the largest amount of Fe (0), followed by sample 2 ( $R=0.6$ ), sample 4 ( $R=8.6$ ), and sample 1 ( $R=0.0$ ). This order has been confirmed by TPR, XPS, EXAFS for both

Pd and Rh systems. The proposed reduction mechanism of the hetero-junction using two semiconducting oxide supports is shown in Scheme 4-2.



**Scheme 4-2** Proposed electron flow cycle in the reduction process of two semi-conductor supports catalyzed by noble metal.

## 4.7 Conclusions

In conclusion,  $\text{ZnFe}_2\text{O}_4\text{-Fe}_2\text{O}_3$  hetero-junction of staggered energy levels using two semiconductor oxide supports has been created to carry out controlled decoration of overlying noble metal NPs with reactive Fe atoms. It is evident that thermally excited holes (as activated oxygen) and electrons are separated on  $\text{ZnFe}_2\text{O}_4$  (higher energy) and  $\text{Fe}_2\text{O}_3$  (lower energy), respectively. Owing to the extended lifetime facilitated by the hetero-junction formation, the holes are allowed to react with the atomic H produced on the noble metal to form water before they recombine with the excited electrons. Meanwhile, the corresponding excited electrons

reduce Fe(III) to Fe(0) at the  $\text{ZnFe}_2\text{O}_4\text{-Fe}_2\text{O}_3$  hetero-junction interface. It is demonstrated that this type of support can be used to tune the composition of supported metal catalysts through a reduction process at mild reaction condition. Since catalytic performance is closely correlated to the composition of active metal phase, such a fine control in metal nanoparticle composition empowers scientists to develop new catalysts with excellent activity and selectivity. This helps to meet the growing demands for greener catalysts.

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# Chapter 5 Catalytic Performance of PdFe and RhFe NPs in Hydrogenolysis of Vicinal Diol Units in Biomass Derived Chemicals

## Overview

The successfully prepared PdFe and RhFe bimetallic NPs are applied in the hydrogenolysis of biomass derived molecules with vicinal diol units. It is demonstrated that the catalytic properties of noble metals (Pd, Rh) can be well tuned by the controllable decoration of Fe atoms reduced from the underneath support. A progressive increase in Fe(0) content of the bimetallic nanoparticles is shown to give more enhanced selectivity of C-C cleavage over C-O cleavage in the vicinal diol with small alcohols as the main products. This provides an opportunity for the synthesis of valuable alcohol molecules from direct biomass utilization. The enhancement of catalytic ability is attributed to the modified electronic structure of noble metals by reactive Fe atoms:

- (i) The *d*-band electron filling of the RhFe or PdFe particles decreases with progressive Fe substitution.
- (ii) The *d*-band center position of the RhFe metallic phase rises with increasing Fe content.
- (iii) In a sharp contrast, for the Pd samples, *d*-band center position only increases slightly at low Fe content but moves dramatically downwards with further Fe decoration.

The catalytic performance varies accordingly which suggests a strong structure-activity relationship in catalysis.

## 5.1 Introduction

Currently, the energy and chemical provisions heavily rely on non-renewable fossil fuels which are neither secured, nor sustainable sources.[1,2] With ever increasing energy demand but continuously lowering of natural reserves, these non-renewable routes are unlikely to last for a long time.[3,4,5,6] Renewable resources, including hydro, wind, solar powers and biomass, are therefore becoming increasingly important for sustainable development.[1] Due to the large contribution to the global primary energy (up to 40% in some countries), biomass is recently advocated as one of the main alternatives in the United National Conference on Environment and Development.[7] The direct use of biomass is, however, limited. Thus, catalytic conversion of biomass molecules to value-added chemicals is required. For example, the conversion of biomass molecules to small alcohol molecules (methanol, ethanol, etc.) in hydrogen is desirable as these volatile high energy density liquids can be widely used for both energy consumption (as transportation fuels) and chemical synthesis.[5] At present, methanol can be produced from biomass industrially by a two steps process: the first step is the gasification of biomass to “synthesis gas” containing CO and H<sub>2</sub>; then CO/H<sub>2</sub> is converted into methanol.[8] However, this process requires a temperature at or above 850 °C to break down the biomass molecules to synthesis gas, followed by its reformation to methanol at 200-250 °C under pressure of 50-100 bar. Therefore, this process is highly energy inefficient. Meanwhile, the production of ethanol from sugarcane and corn by the biological fermentation method is known for several thousands of years, but this process is not only food dependent, but is also very slow.[9-11] As a result, a new and direct transformation of biomass and derived chemicals (cellulose, sugar, glycerol, etc.)

into valuable small alcohol molecules over inorganic based catalyst would be commercially very attractive.[12-16] Most biomass molecules exist in the form of  $-(\text{CH}(\text{OH}))_n-$  chain. Thus, from the viewpoint of molecular structure, the breakdown of these biomass molecules to small alcohol molecules must be achieved through the hydrogenolytic cleavage of C-C bond in  $-\text{CH}(\text{OH})\text{CH}(\text{OH})-$  chain with the vicinal diol units. However, much current research has focused on hydrogenolytic C-O cleavage of biomass or biomass derived molecules for the production of liquid alkanes as fuels. Unfortunately, the rapid C-C cleavage accompanying the C-O cleavage always leads to the formation of undesirable light alkanes.[17,18] There is only limited literature exploring the production of small alcohol molecules directly from biomass, which involves the selective C-C cleavage of vicinal diol units. The development of this catalysis reaction is very challenging since any low selectivity for C-C over C-O cleavage of the catalytic process causes light alkane formation. It also gives a wide product distribution that causes separation problems (note their similar homolytic cleavage energies:  $\Delta H_{\text{C-C}}$  348 kJ mol<sup>-1</sup> and  $\Delta H_{\text{C-O}}$  360 kJ mol<sup>-1</sup>). [19,20] Pd/FeO<sub>x</sub> catalyst containing small supported PdFe bimetallic nanoparticles of low Fe content was reported to be highly active in breaking down ethylene glycol molecule (the simplest biomass related molecule with basic  $-\text{CH}(\text{OH})\text{CH}(\text{OH})-$  unit) in hydrogen, without the production of methane. [19] The liquid products mainly consist of a mixture of methanol (the product of C-C cleavage) and ethanol (the product of C-O cleavage) at comparable quantity, which implies that there is no specific C-C cleavage over C-O cleavage. When it was tested for the hydrogenolysis of glycerol, a range of products, including ethylene glycol, 1, 2-propandiol, 1-propanol, methanol, ethanol, with analogous concentrations, were also obtained. This causes a terrible problem of product separation blocking the industry application. Thus, in order to

produce small alcohol molecules efficiently from biomass substrates, a new catalyst with a high selectivity for C-C over C-O cleavage is needed.

In this chapter, supported PdFe and RhFe bimetallic NPs with enhanced Fe content are employed to pursue higher selectivity towards a specific product. The modification mechanism of Fe atom on Pd structure and the structure-activity relationship in catalysis are also discussed.

## 5.2 Synthesis of materials

The syntheses of PdFe and RhFe bimetallic catalysts employed in this chapter are described in Chapter 3 and Chapter 4. Briefly, ZnO additives were introduced to the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> support at limited quantity. Upon calcination, ZnFe<sub>2</sub>O<sub>4</sub> is formed in excess of Fe<sub>2</sub>O<sub>3</sub> to form a two-phase ZnFe<sub>2</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> support containing a hetero-junction. By varying the ratio of ZnFe<sub>2</sub>O<sub>4</sub>:Fe<sub>2</sub>O<sub>3</sub> and in the presence of noble metal loading (Pd and Rh), the reduction of iron ions into metallic iron atom can be well-tuned. A series of PdFe and RhFe bimetallic NPs with variable compositions were thus prepared at high dispersion. The detailed reduction mechanism was described in Chapter 4.

In this chapter, samples are named by their supports compositions as in Chapter 4; for instance, sample 1 (R=0.0) (R= ZnFe<sub>2</sub>O<sub>4</sub>:Fe<sub>2</sub>O<sub>3</sub>) refers to noble metal supported on iron oxide support without zinc blending. The compositions of the supports are given in Table 5-1.

**Table 5-1** Compositions of the zinc blended iron oxide supports for the noble metal.

| Sample No. | Zn wt% | ZnFe <sub>2</sub> O <sub>4</sub> : Fe <sub>2</sub> O <sub>3</sub> |
|------------|--------|-------------------------------------------------------------------|
| 1          | 0.0    | 0.0                                                               |
| 2          | 11.8   | 0.6                                                               |
| 3          | 13.5   | 1.0                                                               |
| 4          | 20.8   | 8.6                                                               |

## 5.3 Characterization of supported PdFe bimetallic NPs

### 5.3.1 X-ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS)

The XPS curves of Fe 2p for a series of reduced sample are shown in Figure 5-1. The binding energies of Fe 2p<sub>3/2</sub> clearly show a decrease trend, with sample 1 (R=0.0) > sample 4 (R=8.6) > sample 2 (R=0.6) > sample 3 (R=1.0). It is noted that the literature values for Fe(0) 2p<sub>3/2</sub> and Fe<sub>3</sub>O<sub>4</sub> 2p<sub>3/2</sub> are 707.7 eV and 710.2 eV, respectively. [30, 31] Therefore, the lower binding energy implies the lower oxidation state of Fe. For sample 1 (without the addition of zinc), the binding energy of Fe 2p<sub>3/2</sub> is 710.0 eV, which agrees with the literature value of Fe<sub>3</sub>O<sub>4</sub>. The XRD patterns of the reduced samples are displayed in Figure 5-2b; all the diffraction peaks in the pattern of reduced sample 1 can be indexed to Fe<sub>3</sub>O<sub>4</sub>, which also confirms the support is mainly composed of Fe<sub>3</sub>O<sub>4</sub>. For sample 3, the Fe binding energy is much lower than that of Fe<sub>3</sub>O<sub>4</sub> despite the intense diffraction peaks of Fe<sub>3</sub>O<sub>4</sub> in XRD pattern. The XPS curve can be fitted by two peaks at 707.8 eV and 710.7 eV which are assigned to Fe(0) and Fe<sub>3</sub>O<sub>4</sub>, respectively. The strong peak at 707.8 eV in the fitting XPS curve for sample 3 (R=1.0) indicates that the concentration of Fe(0) on the surface of this sample is significantly high. According to the values

of Fe binding energy, the amount of produced Fe(0) orders as sample 1 ( $R=0.0$ ) < sample 4 ( $R=8.6$ ) < sample 2 ( $R=0.6$ ) < sample 3 ( $R=1.0$ ), which is consistent with the reduction result of TPR described in Chapter 4 (section 4.5). Zn(II) will not be reduced in the presence of Fe(II) due to the much more negative reduction potential of Zn(II) to Zn(0) than that of Fe(II) to Fe(0) ( $E^0[\text{Zn(II)/Zn(0)}] = -0.76 \text{ V}$ ,  $E^0[\text{Fe(II)/Fe(0)}] = -0.44 \text{ V}$ ). Thus, with increasing concentration of Zn(II), the diffraction peaks for ZnO ( $31.8^\circ$ ,  $34.4^\circ$ ) become more significant as shown in Figure 5-2b.

Meanwhile, for Pd 3d XPS as shown in Figure 5-2a, the binding energy of Pd 3d is progressively attenuated with increasing amount of Fe(0), which reaches a minimum at sample 3 ( $R=1.0$ ). This can be accounted for by the fact that Fe is more prone to lose its electrons to Pd in their shared electronic bands (electronegativity of 1.8 and 2.2 for Fe and Pd atom, respectively) indicating the strong interaction of Fe and Pd atoms in proximity.

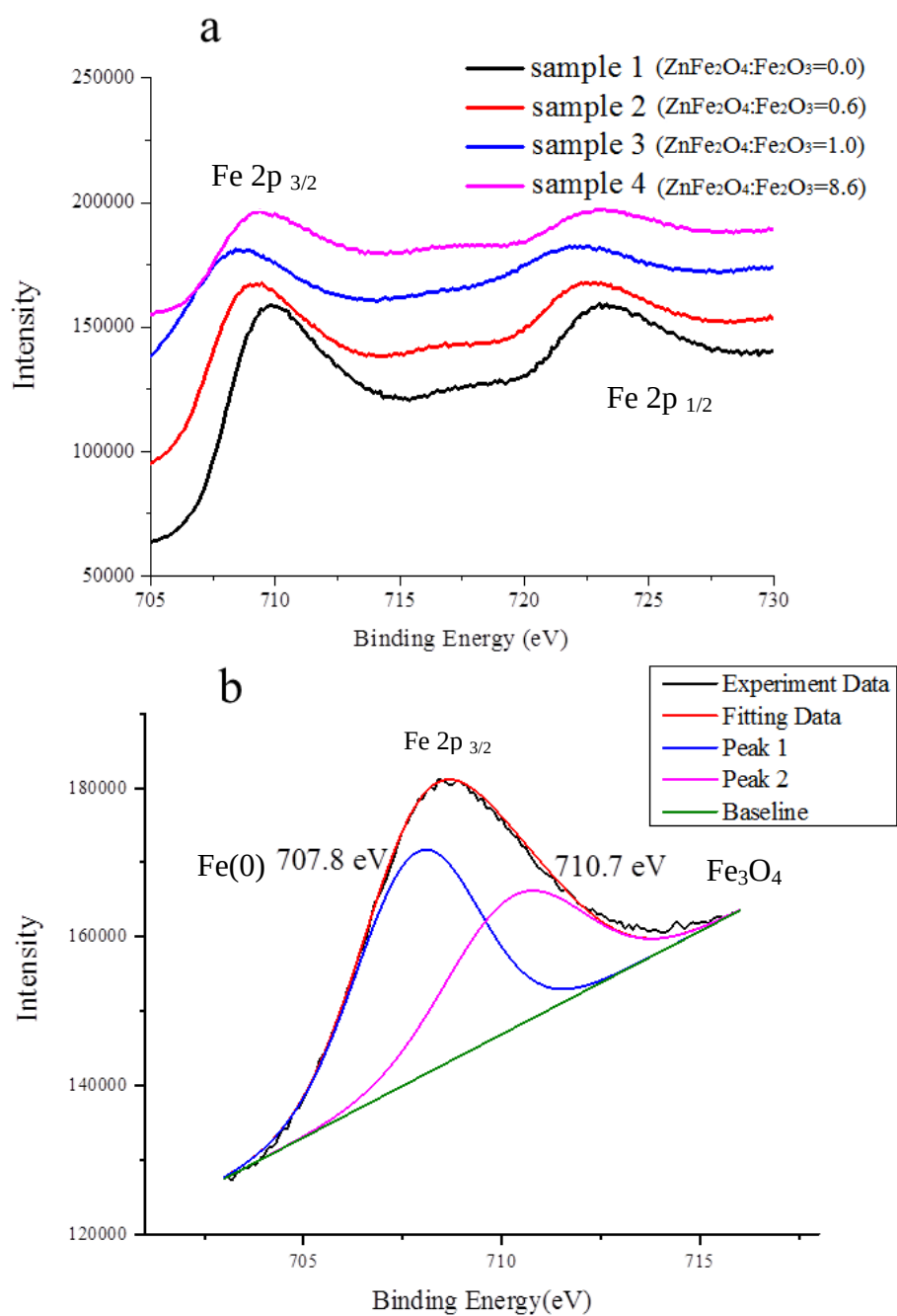


**Figure 5-1** (a) XPS curves of Fe 2p of the reduced samples 1-4; (b) XPS curve fitting of Fe 2p for sample 3 ( $\text{ZnFe}_2\text{O}_4:\text{Fe}_2\text{O}_3=1.0$ ).

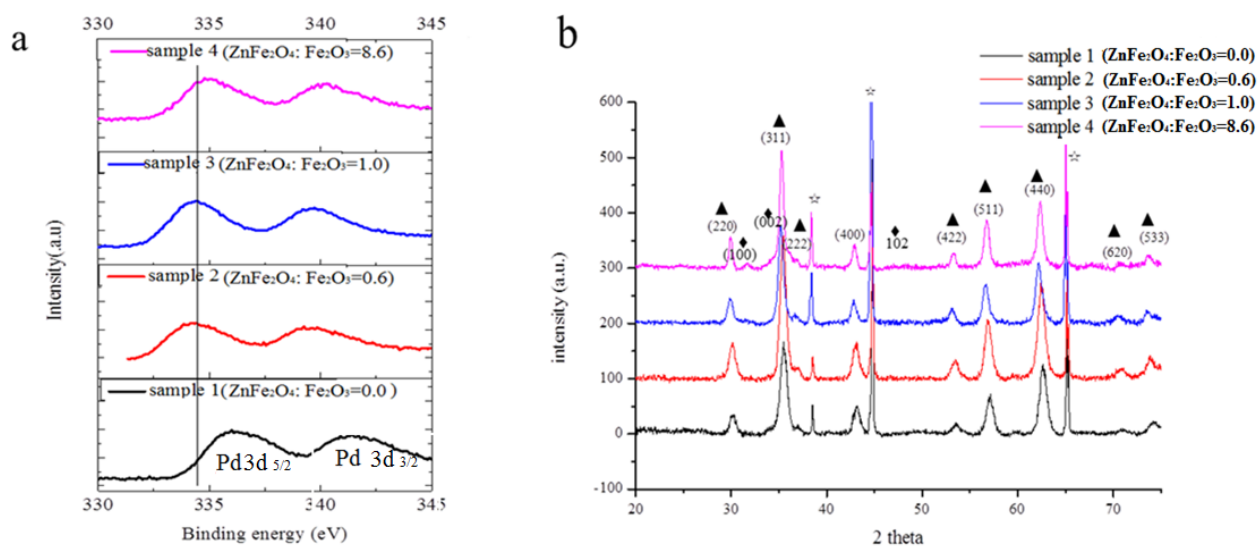


**Figure 5-2** (a) XPS of Pd 3d of the reduced Pd samples 1-4; (b) XRD patterns of the samples after pre-reduction (▲Fe<sub>3</sub>O<sub>4</sub>, ◆ZnO, ☆Al sample holder).

### 5.3.2 Extended X-ray Absorption Fine Structure (EXAFS)

Given the fact that Pd is the active site facilitating the catalytic reduction of Fe ion to Fe(0), supported PdFe bimetallic nanoparticles are expected to be formed at the interface through the interaction of Pd and Fe atoms. The EXAFS results of the samples at Pd K edge are shown in Figure 5-3 and Table 5-2. The total coordination number (CN) (5.3-6.5) of Pd in these samples suggests that the produced metallic Pd containing phase is extremely small in size. The average size of the Pd-based nanoparticles were estimated to be 1.0-1.5 nm from the analysis of the total CN derived by EXAFS data within acceptable R (fitting factor) and Debye-Waller factors, based on the calibration model of a recent EXAFS study.[32,33] Another striking feature in EXAFS is the direct observation of a shorter scattering path at 2.58 Å compared with the typical Pd–Pd distance at 2.70 Å after reduction (kept in inert atmosphere).[34] The distance of 2.58 Å represents the first shell neighbour Fe atoms around each Pd absorbing atom (number of

neighbour Fe ranges from 0.7 to 2.4). Sample 3 (R=1.0) gives the highest number of first shell neighbour Fe to Pd followed by sample 2 (R=0.6) > sample 4 (R=8.6) > sample 1 (R=0.0) reflecting the variable composition of PdFe nanoparticles, which is consistent with the results of TPR and XPS. The experimental and fitting EXAFS curves for all the Pd samples are shown in Figure 5-4.

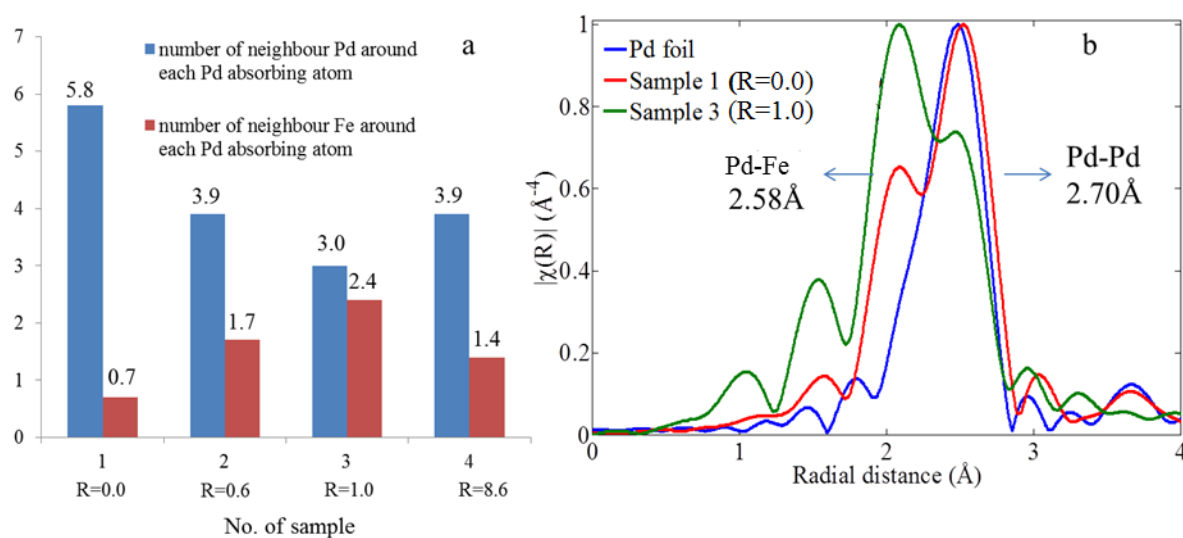
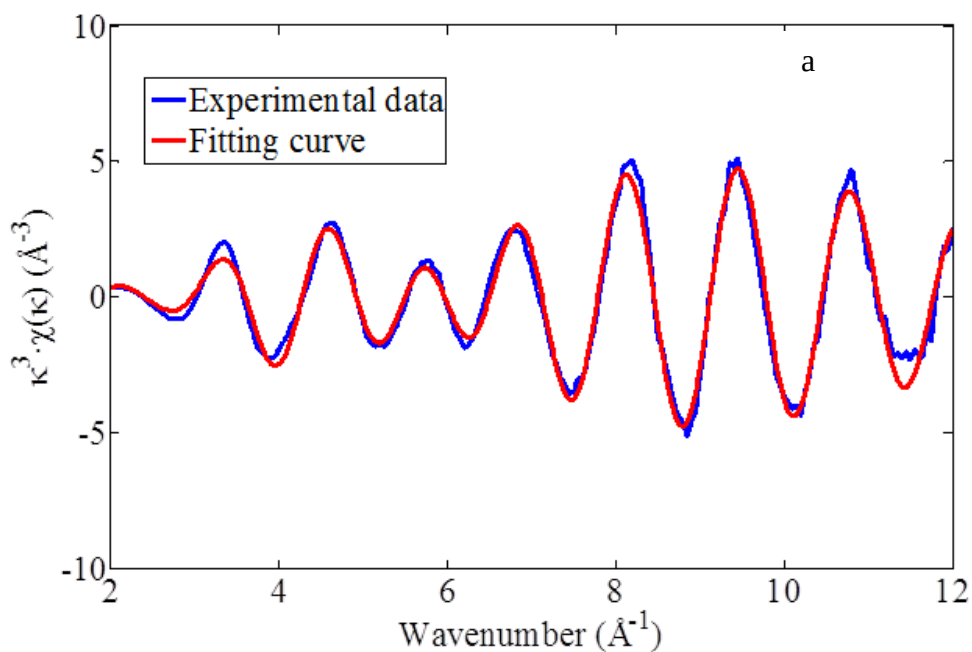


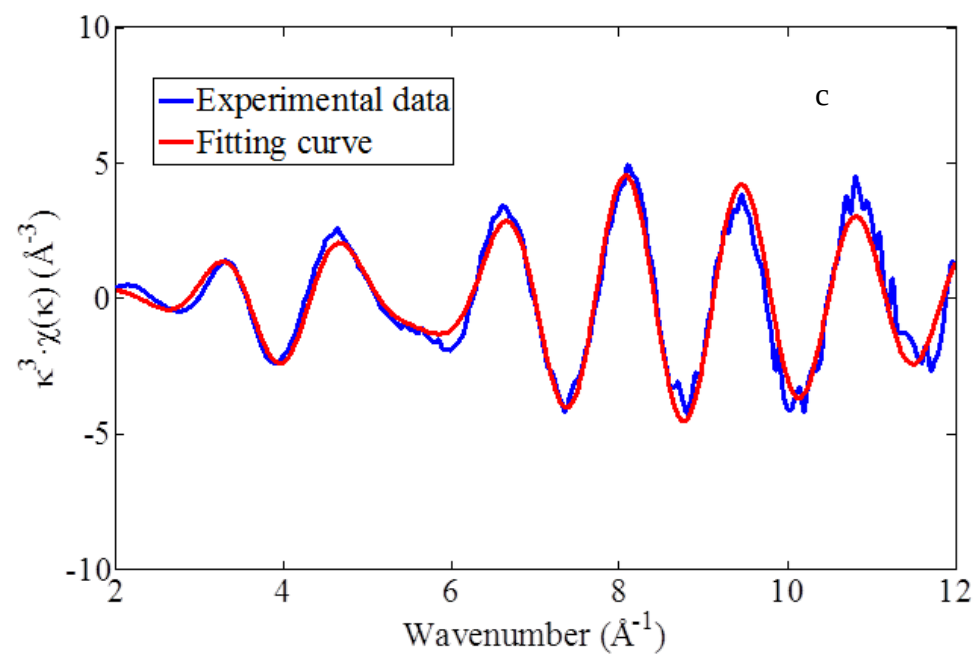
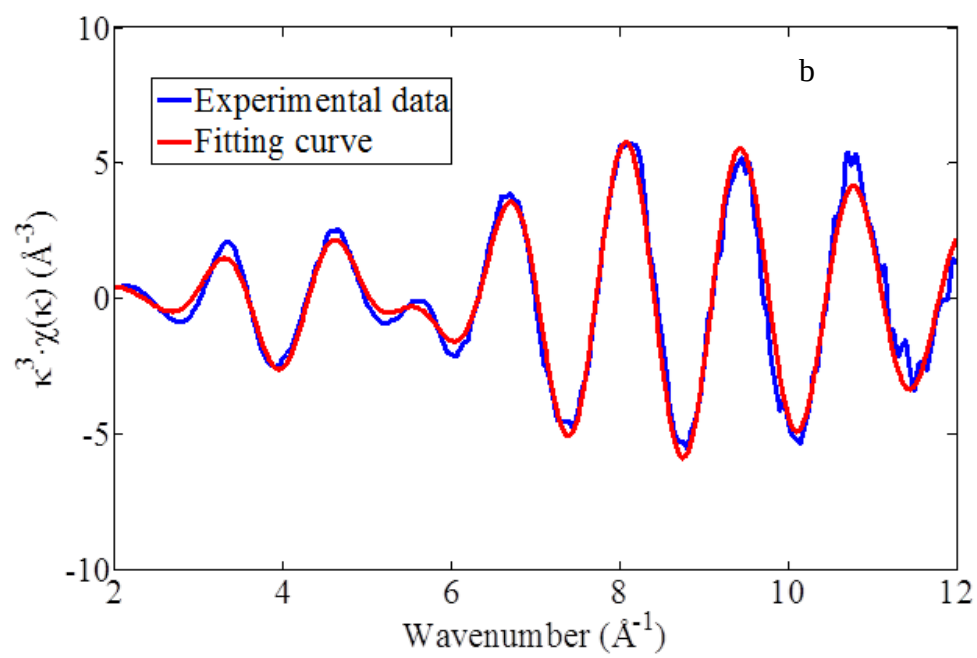
**Figure 5-3** (a) Number of neighbour Pd (NPd) and Fe atoms (NFe) around each Pd absorbing atom derived from EXAFS fittings; (b) the Fourier transform of the EXAFS curves (typical EXAFS curves against Radial distance) for sample 1 (R=0.0) and sample 3 (R=1.0) with a reference of Pd foil.

**Table 5-2** Average coordination environment of a Pd absorbing atom from the EXAFS results for the reduced zinc modified Pd/Fe<sub>2</sub>O<sub>3</sub> samples.

| Sample | Total CN | $\Delta E$ (eV) | Pd-Pd distance (Å) | D-W factor (Å <sup>2</sup> ) | Pd-Fe distance (Å) | D-W factor (Å <sup>2</sup> ) | R    |
|--------|----------|-----------------|--------------------|------------------------------|--------------------|------------------------------|------|
| 1      | 6.5(3)   | 2.0             | 2.70(2)            | 0.009(1)                     | 2.60(1)            | 0.006(1)                     | 0.5% |
| 2      | 5.8(6)   | 1.0             | 2.71(1)            | 0.011(1)                     | 2.56(1)            | 0.006(1)                     | 0.9% |
| 3      | 5.4(6)   | -2.0            | 2.69(1).           | 0.009(1)                     | 2.58(1)            | 0.013(1)                     | 2.5% |
| 4      | 5.3(4)   | 1.1             | 2.71(1)            | 0.014(1)                     | 2.56(1)            | 0.004(1)                     | 0.9% |

(“CN” is coordination number; “ $\Delta E$ ” is the energy difference between the experimental absorption energy and the calculated value in curve fitting; “D-W” is Debye Waller; “R” factor is the indication of the quality of curve fitting)





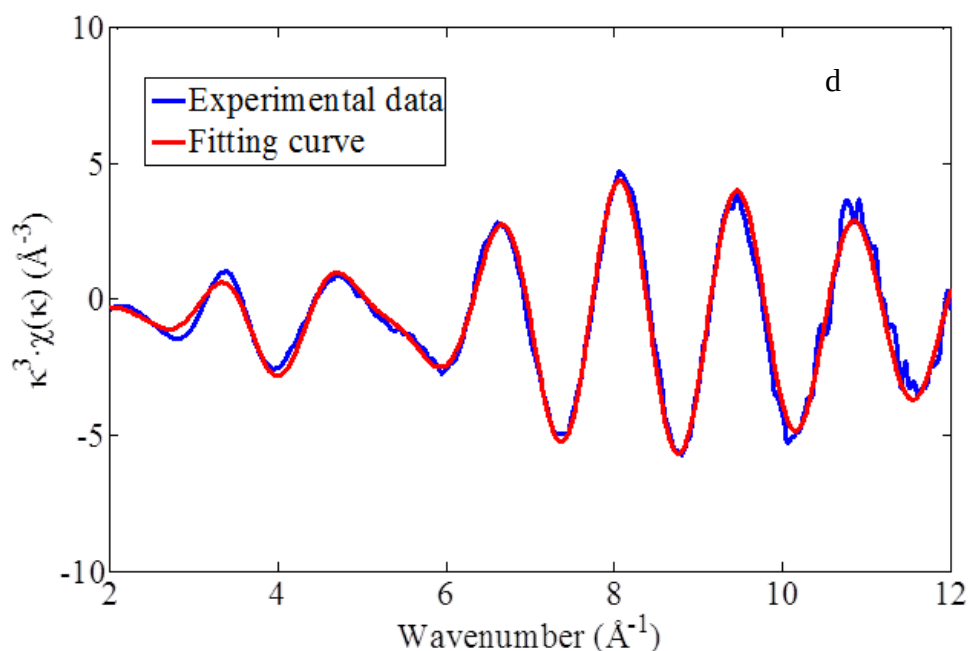


**Figure 5-4**  $k^3$  space EXAFS curves of Pd in (a) sample 1 ( $R=0.0$ ), (b) sample 2 ( $R=0.6$ ), (c) sample 3 ( $R=1.0$ ), (d) sample 4 ( $R=8.6$ ). (blue: experiment data; red: fitting data)

### 5.3.3 Transmission Electron Microscopy (TEM)

TEM was conducted to visualize the Pd containing metal particles. From Figure 5-5, the images show that the structure and the shape of the particles are irregular in the samples 1 ( $R=0.0$ ) and 3 ( $R=1.0$ ) with no significant difference in the morphology. From the high resolution images, clear lattice fringe separations of 0.23 nm of metal particles were found in both of the two samples which can be assigned to the lattice spacing of (111) plane of Pd or PdFe particles. From the particle size distribution, the average size of metal particles is around 1-3 nm (with mean size of 1.5 nm), which is almost the same for the two samples and also consistent with the estimations

from the EXAFS data. The addition of Zn(II) only changes the composition of the supported PdFe nanoparticles without altering the particle size.

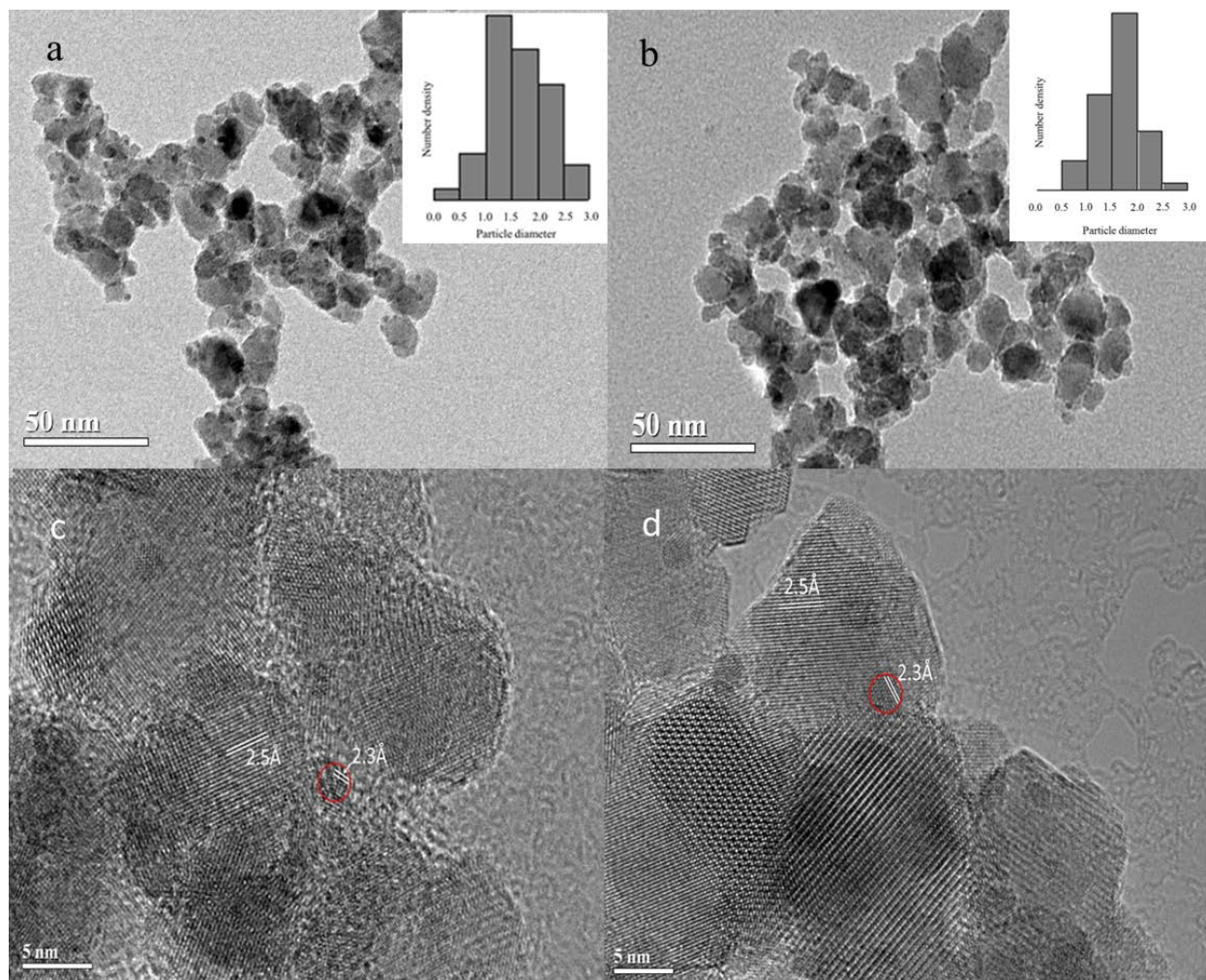


**Figure 5-5** (a, b) TEM and (c, d) HRTEM images for reduced sample 1 (R=0.0) (a,c) and sample 3 (R=1.0) (b,d) (the labelled distance of 2.5 Å corresponds to inter-planar distance of the (311) plane of  $\text{Fe}_3\text{O}_4$  [35]).

### 5.3 Catalytic tests of PdFe and RhFe catalysts in hydrogenolysis of ethylene glycol

The combined results of XPS, EXAFS, TEM demonstrate the successful preparation of supported PdFe and RhFe bimetallic NPs with variable compositions. This is achieved from the controllable reduction of ZnFe<sub>2</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> hetero-junction support in the presence of a noble metal such as Pd or Rh. The catalytic properties of these supported RhFe and PdFe bimetallic clusters for the hydrogenolysis of ethylene glycol (EG) have been studied. This reaction is usually considered as an important model reaction for the catalytic transformation of biomass molecules with basic -CH(OH)CH(OH)- units. The detailed procedures of catalytic tests were described in Chapter 3. The conversion, product selectivity and the value of “Selective C-C cleavage/Selective C-O cleavage” are calculated as following:

$$\text{Conversion} = \frac{\text{moles of substrate before reaction} - \text{moles of substrate after reaction}}{\text{moles of substrate before reaction}}$$

$$\text{Selectivity} = \frac{\text{moles of specific product} * \text{its mole carbon number}}{\sum \text{moles of each product} * \text{its mole carbon number}}$$

$$\frac{\text{selective C - C cleavage}}{\text{selective C - O cleavage}} = \frac{\frac{\text{moles of substrate consumed to produce the selective C - C cleavage product}}{\text{moles of substrate consumed to produce the selective C - O cleavage product}}}{1}$$

The detailed catalytic performances of Rh and Pd-based catalysts are summarized in Table 5-3 and Figure 5-6. Methanol, ethanol, CH<sub>4</sub> and CO<sub>2</sub> are detected as the major products. From the thermodynamic diagram of the system as shown in Figure 5-7, CH<sub>4</sub> and CO<sub>2</sub> as the main equilibrium components are regarded as the thermodynamically controlled products. They are produced by the breakage of all the bonds in ethylene glycol followed by extensive

hydrogenation reaction or steam reforming, respectively. [36] On the other hand, methanol and ethanol are the kinetic controlled products. It is noted that from Figure 5-6 that the selectivity for these alcohols greatly varies with the increase in number of neighbour Fe atoms for Pd or Rh derived from the EXAFS data (NFe). For Rh samples, both methanol and ethanol selectivities rise with the increasing Fe content in the bimetallic phase. For Pd samples, only the methanol selectivity increases with Fe decoration, while the ethanol selectivity shows the opposite trend. Meanwhile, the total alcohol selectivity in Pd system is much higher than that in Rh system. The significant variation in catalytic performance is ascribed to the different electronic structure of noble metals.

**Table 5-3a** Catalytic performance of the supported RhFe catalysts in hydrogenolysis of ethylene glycol (EG). (0.25 g catalyst; 30 mL EG solution (5 wt%); 50 bar H<sub>2</sub> (r.t.); 250 °C for 12 h, the other trace products include CO, C<sub>2</sub>H<sub>6</sub>, etc.)

| Catalyst                             | Conversion % | CH <sub>3</sub> OH selectivity % | C <sub>2</sub> H <sub>5</sub> OH selectivity % | CO <sub>2</sub> selectivity % | CH <sub>4</sub> selectivity % | Total alcohol selectivity % |
|--------------------------------------|--------------|----------------------------------|------------------------------------------------|-------------------------------|-------------------------------|-----------------------------|
| <b>Sample 1</b><br>( R=0.0, NFe=3.6) | 81.7         | 11.3                             | 2.6                                            | 1.3                           | 84.0                          | 13.9                        |
| <b>Sample 2</b><br>(R=0.6, NFe=4.2)  | 23.6         | 18.3                             | 5.3                                            | 12.8                          | 38.0                          | 23.6                        |
| <b>Sample 3</b><br>(R=1.0, NFe=5.2)  | 36.4         | 20.5                             | 7.6                                            | 13.0                          | 63.0                          | 28.1                        |
| <b>Sample 4</b><br>(R=8.6, NFe=3.8)  | 13.7         | 16.0                             | 3.3                                            | 41.9                          | 59.0                          | 19.3                        |

**Table 5-3b** Catalytic performance of the supported PdFe catalysts in hydrogenolysis of ethylene glycol (EG) (0.50 g catalyst; 30 mL EG solution (5 wt%); 50 bar H<sub>2</sub> (r.t.); 250 °C for 24 h, the other trace products include CO, C<sub>2</sub>H<sub>6</sub>, etc.)

| Catalyst                             | Conversion % | CH <sub>3</sub> OH selectivity % | C <sub>2</sub> H <sub>5</sub> OH selectivity % | CO <sub>2</sub> selectivity % | CH <sub>4</sub> selectivity % | Total alcohol selectivity % |
|--------------------------------------|--------------|----------------------------------|------------------------------------------------|-------------------------------|-------------------------------|-----------------------------|
| <b>Sample 1</b><br>( R=0.0, NFe=0.7) | 31.8         | 32.9                             | 14.5                                           | 52.0                          | 0.6                           | 47.4                        |
| <b>Sample 2</b><br>(R=0.6, NFe=1.7)  | 21.0         | 44.7                             | 3.0                                            | 48.3                          | 2.4                           | 47.7                        |
| <b>Sample 3</b><br>(R=1.0, NFe=2.4)  | 23.0         | 52.4                             | 3.2                                            | 42.7                          | 2.1                           | 55.6                        |
| <b>Sample 4</b><br>(R=8.6, NFe=1.4)  | 18.0         | 44.2                             | 4.4                                            | 47.0                          | 0.4                           | 48.6                        |

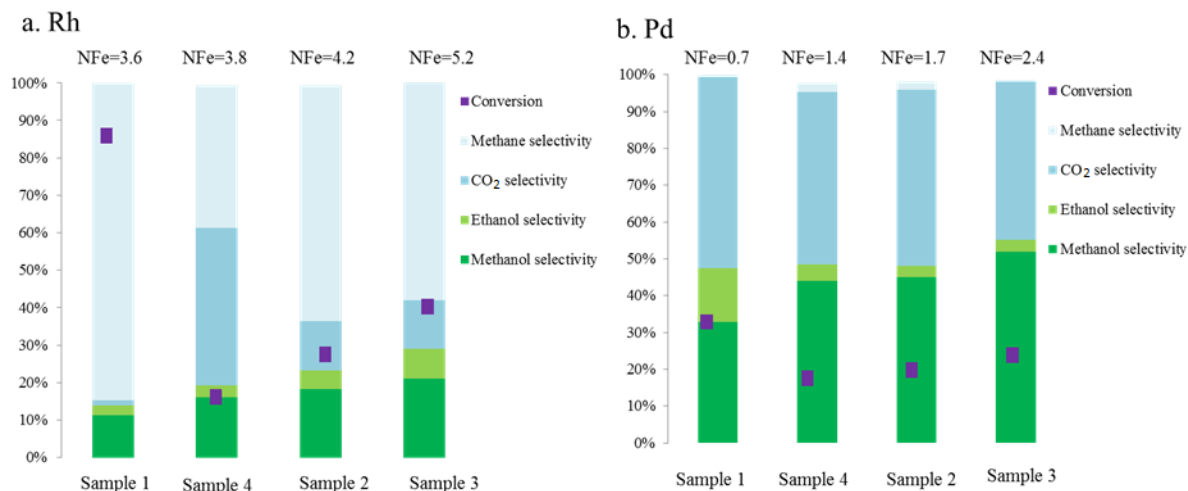


**Figure 5-6** Catalytic performances of (a) Rh samples and (b) Pd samples in hydrogenolysis of ethylene glycol (50 bar H<sub>2</sub>, 250 °C, the trace products include CO, C<sub>2</sub>H<sub>6</sub>, etc.).

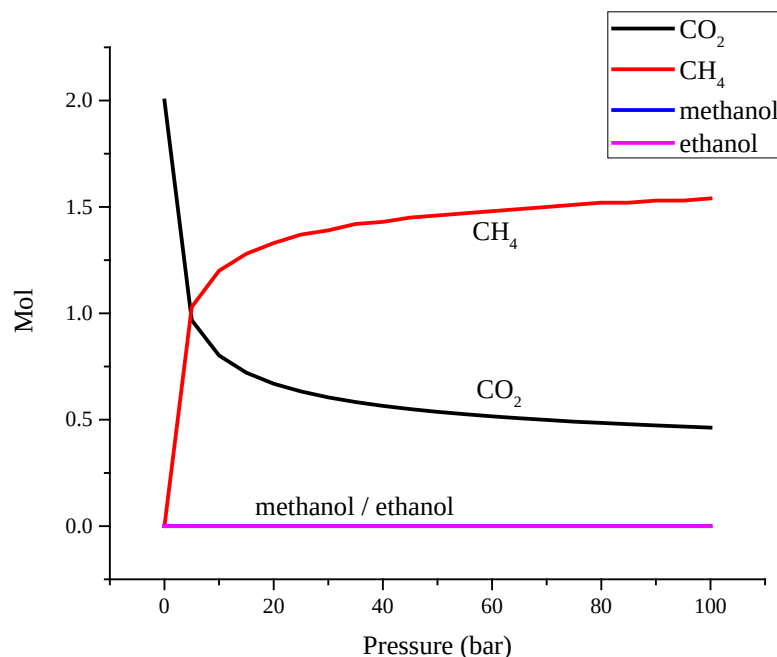


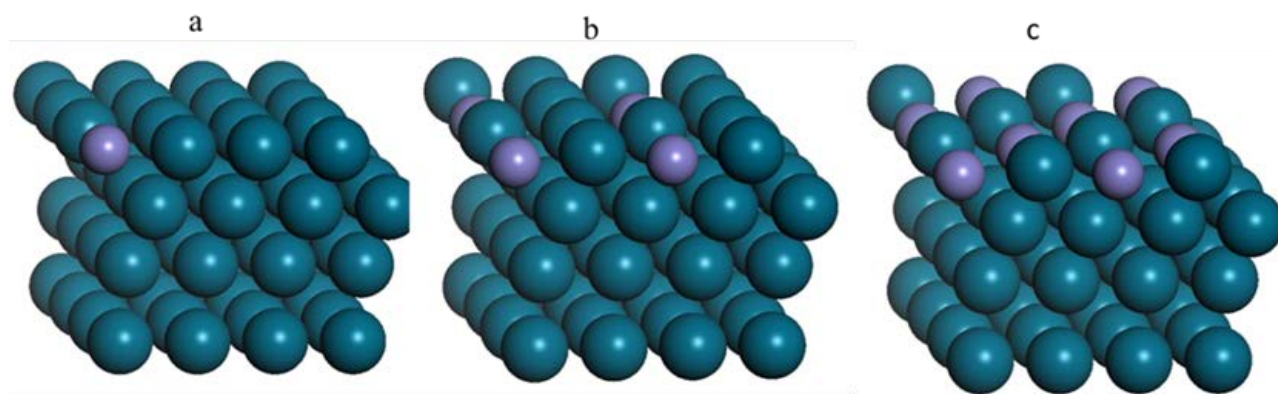
**Figure 5-7** Calculated thermodynamic equilibrium composition diagram (by HSC Chemistry 5.11 thermodynamic calculation software) for the hydrogenolysis of ethylene glycol at 250 °C with varying pressure (starting materials: 1 mol ethylene glycol, 2 mol H<sub>2</sub>, 63 mol H<sub>2</sub>O. The ratio of H<sub>2</sub>O: ethylene glycol is obtained from the composition of the substrate solution.)

## 5.4 Density Function Theory (DFT) modeling calculation

### 5.4.1 Modeling method

DFT method was used to investigate the electronic structure of PdFe and RhFe bimetallic NPs. And the calculations were finished with collaboration of Dr. Jin Qu from our group. All calculations were performed in the framework of DFT by using the Vienna *ab initio* simulation package (VASP 4.6). [21-24] The projector-augmented wave (PAW) potentials [25, 26] were used for the core electron interaction. The Perdew–Burke–Ernzerhof (PBE) [27, 28] based on the generalized gradient approximation (GGA) was employed to evaluate the non-local exchange-

correlation energy. A plane wave basis set with a cut-off energy of 350 eV was used. For structure optimization, the ionic positions were allowed to relax until the forces became less than 0.05 eV Å<sup>-1</sup>. Spin polarization was included for all the calculations. The most abundant close-packed Pd(111) surface was modelled by a periodic slab model with four layers of metals. A 4×4 surface unit cell (11.171× 11.171 Å<sup>2</sup>) and a 3×3×1 k-point grid determined by the Monkhorst-Pack method were utilized in this study. The bottom layer was fixed during all geometry optimizations. A vacuum layer of 15 Å along the z direction perpendicular to the surface (the x and y directions parallel to the surface) was employed to prevent spurious interactions between the repeated slabs. Some Fe impurities were induced to substitute for surface Pd or Rh atoms to study the modification effects on Pd(111) or Rh(111). The non-segregated surface alloy model [29] was used here as showed in Scheme 5-1.



**Scheme 5-1** Surface alloy models: (a) M<sub>15</sub>Fe; (b) M<sub>3</sub>Fe; (c) MFe. (blue balls: noble metal atoms M (M=Rh, Pd), purple balls: Fe atoms)

#### 5.4.2 Results of modelling computation

It is shown in Figure 5-8c, d that *d*-band electron filling of the RhFe or PdFe particles decreases with progressive Fe substitution. This is due to the relatively lower *d* electron density of Fe (3d<sup>6</sup>)

than those of the noble metals (Rh 3d<sup>8</sup> Pd 3d<sup>10</sup>). Also, the variation of PdFe at increasing Fe content gives a greater slope than that of RhFe owing to the larger difference in d electron density between Pd and Fe atom. It is also interesting to find that the *d*-band center positions of the RhFe metallic phase rise with increasing Fe content due to the mixing with the higher energy orbital of Fe 3d than that of Rh 4d. In a sharp contrast, for the Pd samples, the *d*-band center position only increases slightly at one Fe atom substitution according to our model but moves dramatically downwards at higher content of Fe despite the incorporation of the higher energy level Fe orbital (3d) into Pd (4d). This is attributed to the overriding effect of decreasing *d*-band filling at greater extent over the up-shifting in energy level of hybrid *d*-band in PdFe. The corresponding density of states (DOS) diagrams for PdFe and RhFe samples with variable Fe content are displayed in Figure 5-9.

Correlating the modelling calculation results with the catalytic performance, it is interesting to observe methanol selectivity exhibits the same variation with the reduction of *d*-band filling versus the content of Fe and ethanol selectivity of the catalysts increases with *d*-band center position of the bimetallic NPs for both Rh and Pd systems (Figure 5-8).

From molecular configuration, methanol is the product of hydrogenolytic C-C bond cleavage of EG, while ethanol is produced through the partial hydrogenolytic C-O bond breakage. And it is envisaged that the 1, 2-diol molecule is adsorbed on the surface of bimetallic nanoparticles through the interaction of its -C-O- functional group with the *d*-band of the noble metal as shown in Scheme 5-2. As the concentration of Fe atom increases, the decreasing *d*-band filling will strengthen electronic  $\sigma$  donation from the weakly  $\sigma^*$  orbital (located on C atom) of EG to noble metal, which enhances the M-C (M=Pd, Rh) bond and hence breaks the C-C bond more favourably as shown below in Scheme 5-2. Thus, methanol selectivity increases with respect to

the decreasing *d*-band filling by the Fe substitution for both Rh and Pd samples. On the other hand, the *d*-band of RhFe at higher position with progressive Fe substitution is expected to match better with the  $\pi^*$  orbital of -C-O- group in EG and enhance the  $\pi$  back donation from RhFe to the empty  $\pi^*$  orbital of substrate, leading to the breakage of the C-O bond and hence increasing ethanol selectivity. In contrast, for the Pd samples, *d*-band center position only increases slightly at one Fe atom and then moves dramatically downwards at higher content of Fe. Consequently, ethanol selectivity for Pd samples decreases with progressive Fe substitution.

The variation of catalytic performance reflects the fine tuning of the catalytic properties of noble metal by the decoration of Fe atoms which is enabled by controlled reduction of  $\text{ZnFe}_2\text{O}_4\text{-Fe}_2\text{O}_3$  hetero-junction support. Although the selectivity for the two alcohols produced from ethylene glycol hydrogenolysis, catalyzed by supported PdFe and RhFe NPs, is not yet sufficient to justify any immediate application, the concept for this fine control in catalyst materials using dual support system is clearly demonstrated.

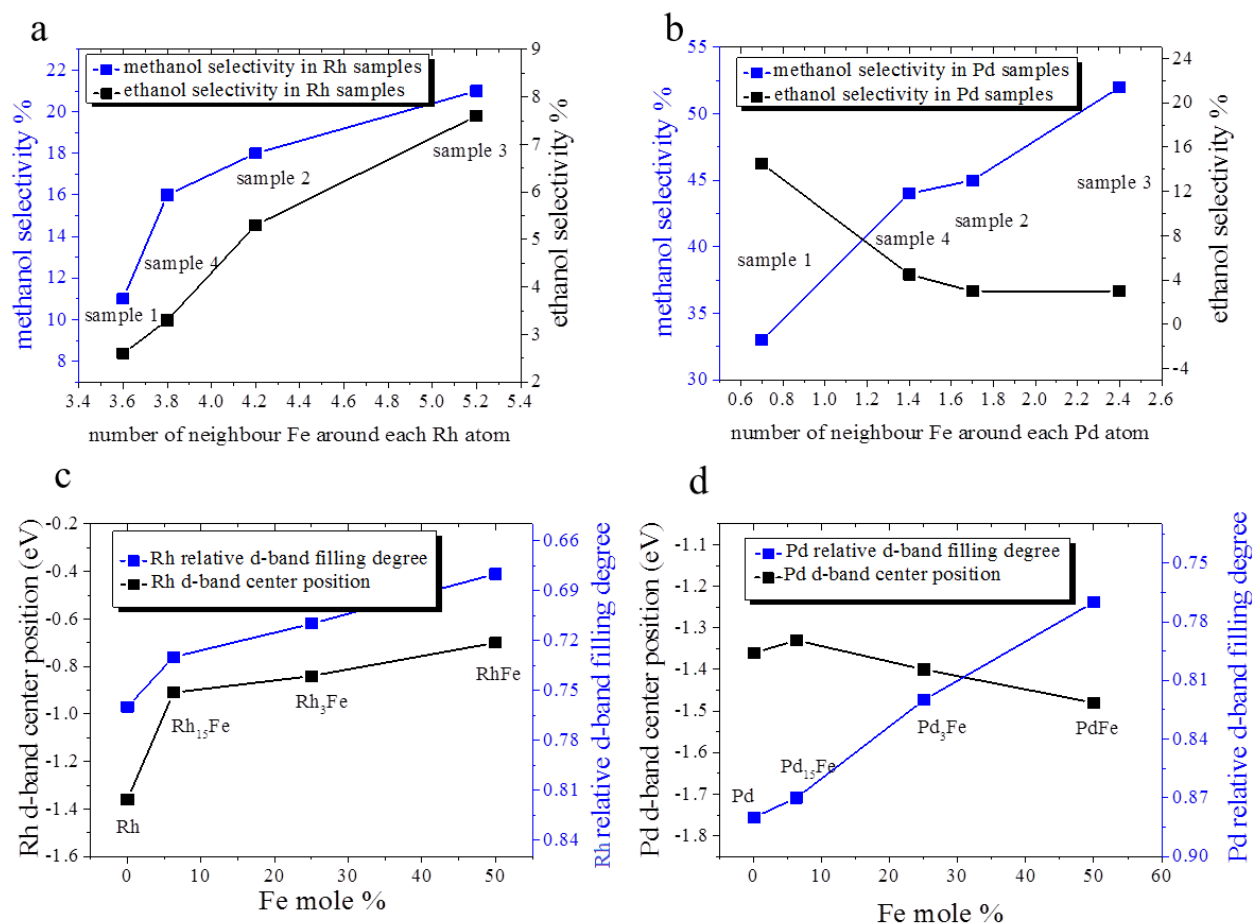


**Figure 5-8** Methanol and ethanol selectivity in hydrogenolysis of ethylene glycol for (a) Rh samples and (b) Pd samples (50 bar H<sub>2</sub>, 250 °C) with variable Fe content (N<sub>Fe</sub> around Pd or Rh); the calculated *d*-band center position and relative *d*-band filling degree for a series of (c) Rh and (d) Pd samples.

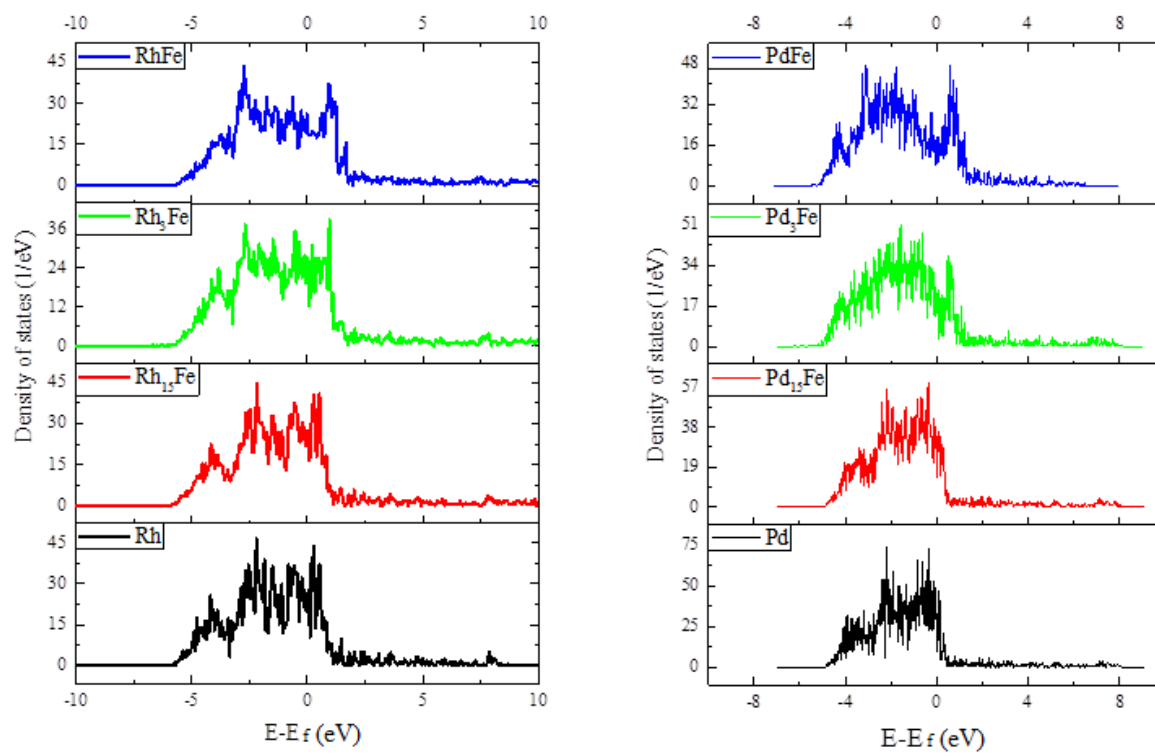
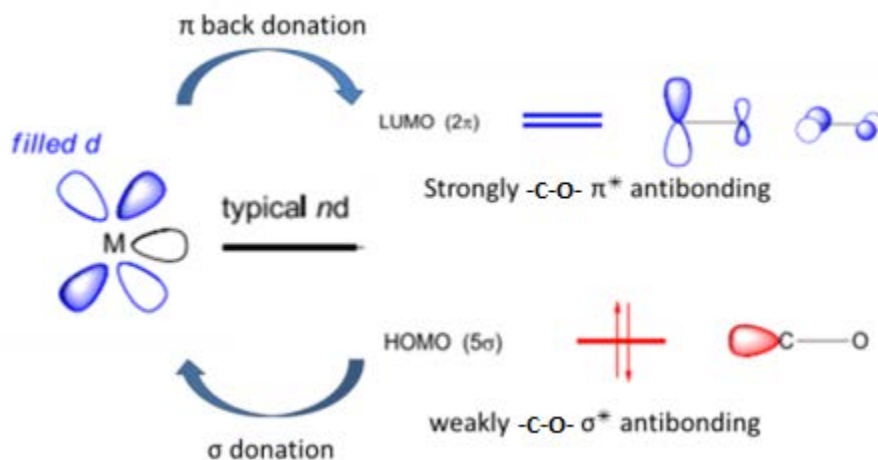


**Figure 5-9** Calculated surface density of states (DOS) diagrams of Pd, Pd<sub>15</sub>Fe, Pd<sub>3</sub>Fe, PdFe and Rh, Rh<sub>15</sub>Fe, Rh<sub>3</sub>Fe, RhFe ( $E_f$  represents the energy level of Fermi level).



**Scheme 5-2** Proposed interactions of noble metal and  $-C-O-$  functional group of biomass molecules.

It is noted that the  $d$ -band center positions of RhFe samples are much higher than those of PdFe samples. Thereby, the adsorption of ethylene glycol on RhFe surface is strong enough to break both C-C and C-O bond simultaneously giving production of  $CH_4$  and  $CO_2$ . As observed, the selectivity of  $CH_4$  and  $CO_2$  is higher than that of methanol and ethanol (the product of selective breakage of C-C bond and C-O bond). While the PdFe catalyst with lower  $d$ -band center position give higher alcohol selectivity and thus is regarded as a more promising catalyst in biomass utilization than Rh samples.

## 5.5 The application of PdFe bimetallic catalyst in a series of biomass derived molecules

### 5.5.1 Hydrogenolysis of vicinal diol molecules by PdFe

Owing to the decreasing  $d$ -band filling and  $d$ -band center position of PdFe with progressive Fe substitution, the methanol selectivity increases at the expense of ethanol selectivity in

hydrogenolysis of EG. This suggests the specificity of Pd for cleavage of C-C bond over C-O bond is raised progressively by increasing Fe decoration. The value of “Selective C-C cleavage: Selective C-O cleavage” for the PdFe catalysts can be calculated from the mole ratio of methanol to ethanol in the liquid products. As shown in Figure 5-10, the value increases almost linearly with the concentration of Fe(0) in PdFe until it levels off at 16.4 in sample 3 (R=1.0) with the highest Fe(0) content; this means that the selectivity of C-C cleavage in the reaction reaches 95% (16.4/17.4) and methanol can be produced almost exclusively in the final liquid products. The extremely high value of “Selective C-C cleavage: Selective C-O cleavage” for sample 3 (R=1.0) clearly displays its strong catalytic ability in selective breakage of C-C bond over C-O bond in the hydrogenolysis of EG. The 40% CO<sub>2</sub> selectivity reflects a rapid hydrolytic cleavage of the vicinal diol due to the high temperature used to increase the yield of methanol.

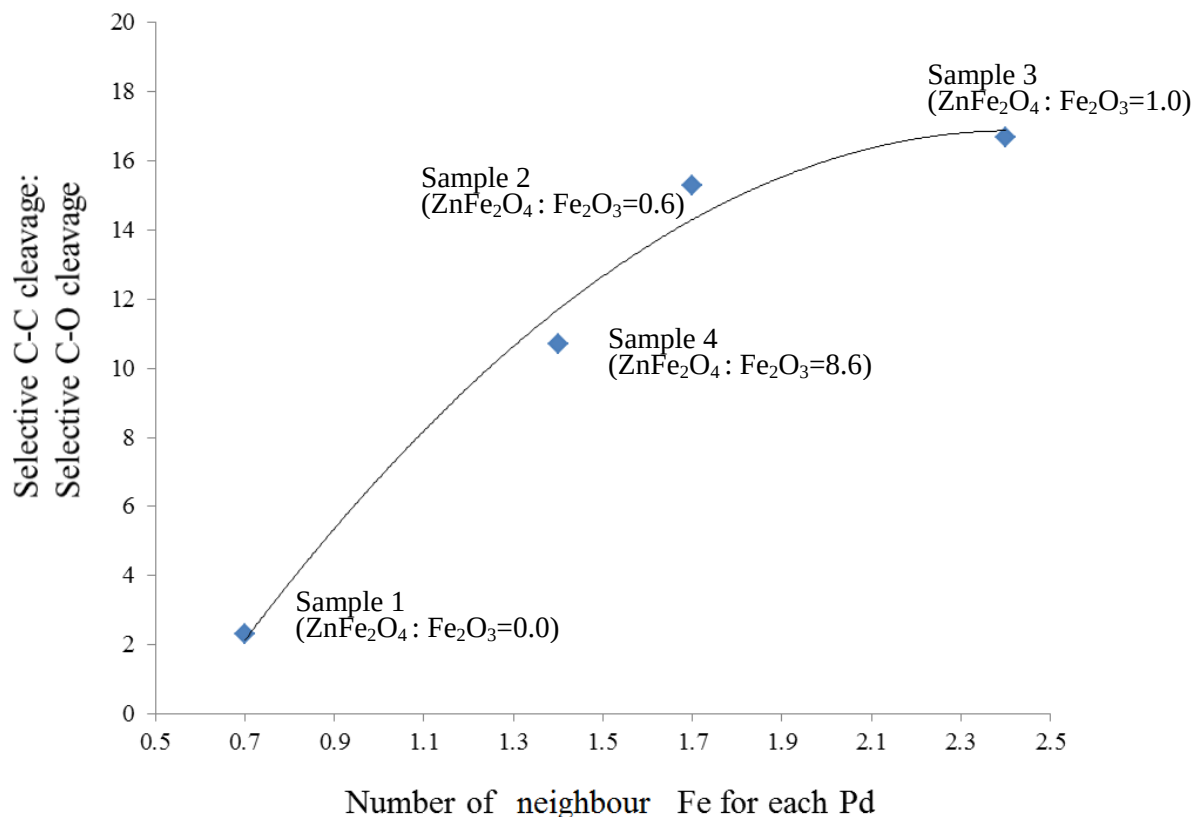


**Figure 5-10** Calculated “Selective C-C cleavage: Selective C-O cleavage” values during hydrogenolysis of EG at increasing Fe content in PdFe. (NFe refers to the number of neighbour Fe around each Pd absorbing atom.)

To explore the generality of this interesting catalytic property, this novel Pd catalyst (sample 3 (R=1.0) was also tested for the hydrogenolysis of 1, 2-propanediol (1, 2-PD) and 1, 2-butanediol (1, 2-BD). The results are summarized in Figure 5-11. In the system of 1, 2-PD, ethanol (EtOH) is the product of hydrogenolytic C-C cleavage while 1-propanol (1-PrOH) is produced by breaking C-O bond. By applying the same principle, 1-propanol is produced by the C-C bond cleavage in the hydrogenolysis of 1, 2-butanediol (1, 2-BD) while butanol (BuOH) is the unique product of the C-O bond breakage. From the mole ratio of the products, the value of “Selective C-C cleavage: Selective C-O cleavage” can be calculated in all the systems. As shown in Table

5-4, the cleavage of C-C/C-O values vary from 16.4 to 3.2 and 60.3 for EG, 1,2-PD and 1,2-BD respectively. The much lower value for 1, 2-PD than the other two is thought to reflect the rapid degradation of the 1, 2-PD on the acidic/basic support through the dehydration of the secondary –OH. [37,38,39] This process involves the formation of C=C bond with the neighbour –CH<sub>3</sub>, followed by hydrogenation on the metal surface to 1-propanol. The inability of C=C formation due to the absence of neighbour –CH<sub>3</sub> in EG and the steric effect of –CH<sub>2</sub>CH<sub>3</sub> in 1, 2-BD disfavours this C-O cleavage on the support and hence the much higher selectivity in C-C cleavage is observed. Overall, the cleavage of C-C/C-O values are much larger than 1, revealing the superior specificity of sample 3 (R=1.0) for selectively breaking C-C bond over C-O bond in the hydrogenolysis of 1, 2 vicinal diols of this series of biomass related molecules.

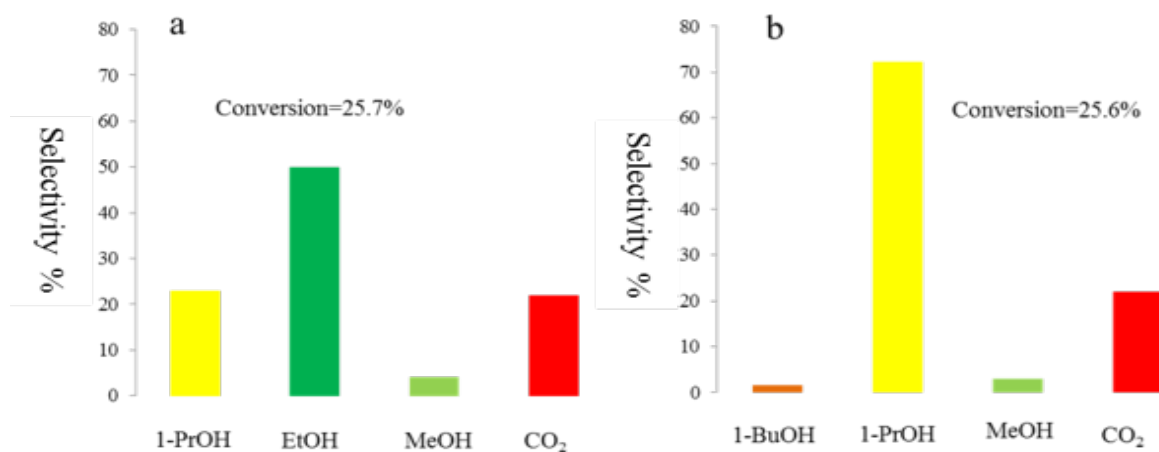


**Figure 5-11** Catalytic performance of sample 3 (R=1.0) in hydrogenolysis of (a) 1, 2-propanediol (1, 2-PD) and (b) 1, 2-butandiol (1, 2-BD) (0.50 g catalyst; 30 mL substrate solution (5 wt%); 50 bar H<sub>2</sub> (r.t.); 250 °C for 24h, trace products include CO, C<sub>2</sub>H<sub>6</sub>, etc).

**Table 5-4** The calculated ratio of “Selective C-C cleavage: Selective C-O cleavage” for sample 3 (R=1.0) in the hydrogenolysis of a series of diols.

| Substrate                   | EG   | 1,2-PD | 1,2-BD |
|-----------------------------|------|--------|--------|
| Selective cleave of C-C/C-O | 16.4 | 3.2    | 60.3   |

### 5.5.2 Hydrogenolysis of glycerol by PdFe bimetallic NPs

The catalytic hydrogenolysis of glycerol by sample 3 (R=1.0) has also been studied. In biodiesel synthesis, glycerol is a well-known by-product. [40] Due to its narrow range of application, glycerol is regarded as an industry waste. [41,42] Thus, the catalytic conversion of glycerol to value-added chemicals is of significant interest from both scientific and technological perspectives. The catalytic result of sample 3 (R=1.0) for glycerol hydrogenolysis is displayed in Figure 5-12. The liquid products identified are mainly composed of 1, 2-PD and EtOH, accompanied by a small proportion of 1-propanol and methanol. The distribution of the liquid products is much narrower than that which is catalysed by the reported PdFe catalyst with a much lower Fe content (Figur 5-12b). [19] It is well accepted that glycerol can be rapidly converted into 1, 2-PD through the dehydration of glycerol on a oxide support, followed by a hydrogenation on metal site (the glycerol conversion as described in Figure 5-12 is 100%). [37,43] Further products are mainly derived from the subsequent breaking down of 1, 2-PD. Taking the final selectivity of EtOH (31.5%) and 1-PrOH (6.2%) into account, the value for “Selective C-C cleavage: Selective C-O cleavage” is 7.6 for sample 3 (R=1.0). This value is even higher than that (3.2) using 1, 2-PD as the substrate. This is presumably because C-C bond is readily cleaved on the metal surface once 1, 2-PD or derivatives are produced, with a minor

effect of the dehydration of the produced diol on the support. In this case, some methanol molecules have been produced in the process of C-C cleavage. Thus, the total selectivity for small alcohol molecules, as the liquid fuel products from glycerol hydrogenolysis - including methanol and ethanol - is over 50% in liquid products when sample 3 is employed as the catalyst. As far as we are aware, the selective catalytic hydrogenolysis of glycerol to these small alcohols as mentioned above for energy utilization has not been reported. The increase of reaction time will further convert 1,2-PD, which subsequently increases the selectivity of small alcohol molecules.

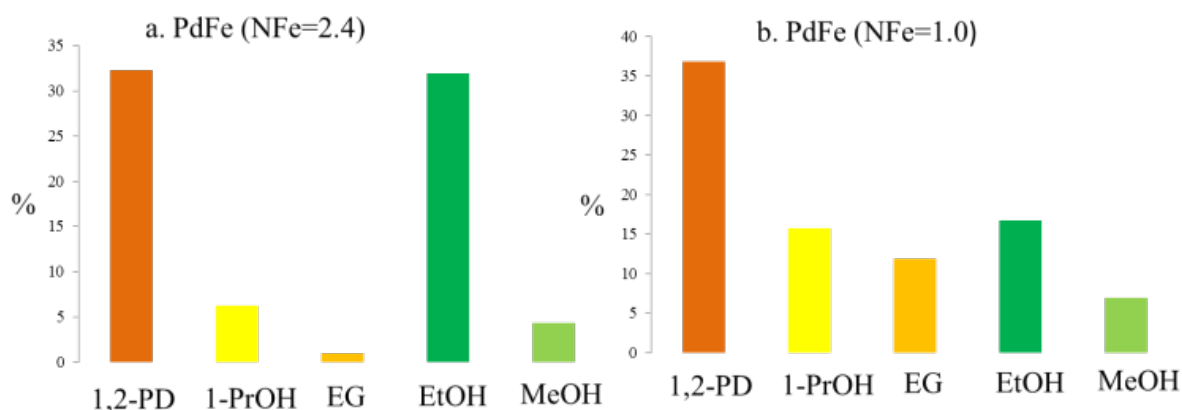


**Figure 5-12** Catalytic performance of (a) sample 3 (R=1.0) and (b) the reported PdFe catalyst in reference 19 in hydrogenolysis of glycerol with 100% conversion. (0.50 g catalyst; 30 mL glycerol solution (1 wt%); 50 bar H<sub>2</sub> (r.t.); 160 mL autoclave with stirring; temp. = 250 °C for 120h, trace products include CO, C<sub>2</sub>H<sub>6</sub>, etc.)

## 5.6 Conclusion

The prepared PdFe and RhFe bimetallic NPs of controllable composition are applied in the hydrogenolysis of ethylene glycol which is a biomass derived molecule. With increasing Fe content, both the positions of *d*-band filling and *d*-band center of PdFe decrease, which

strengthen the electron donation from the biomass substrate to Pd and simultaneously weaken the C-C bond. As a result, an increasing specificity for breaking C-C bond over C-O bond in diol adsorption can be achieved. While for RhFe samples, with incorporation of Fe atoms, the *d*-band center position rises accompanied by the lowering in *d*-band filling. Thereby, the high position of RhFe *d*-band center strengthens the adsorption of ethylene glycol on RhFe surface so that C-C and C-O bonds are cleaved simultaneously. CH<sub>4</sub> and CO<sub>2</sub> are observed as the main products at the expense of methanol and ethanol. Thus, PdFe with a high Fe content is regarded as a more promising catalyst in biomass utilization. It is shown that the catalytic properties of these novel PdFe NPs can be tuned for variable degrees of C-C and C-O cleavage of a series of vicinal 1, 2-diols and glycerol, which is dependent on the Fe content. This may provide a new synthesis capability for the production of small alcohols as fuel molecules from selective hydrolytic fragmentation of large biomass molecules.

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# **Chapter 6 Tunability of Catalytic Properties of Pd-based Catalysts for Hydrogenolysis of Ethylene Glycol Units in Biomass Molecules**

## **Overview**

To increase the utilization and diversify the catalytic conversion routes of biomass resource, the catalytic properties of Pd in hydrogenolysis of ethylene glycol (EG) unit have been thoroughly and systematically investigated. With decoration of various modifier atoms from the reduction of supports, a series of extremely small Pd bimetallic NPs with tunable composition was prepared. It is shown that the catalytic performance of Pd can be fine-tuned from selective C-C cleavage to selective C-O cleavage in the hydrogenolysis of EG by employing various Pd-based bimetallic NPs as catalysts. From PdZn, PdNi, PdCo to PdFe, the selectivity of C-C cleavage rises from 44% to 95%, corresponding to the decreasing *d*-band filling of Pd. With decoration of Co atoms at high content, the *d*-band center position of Pd was raised significantly and PdCo was confirmed to be active and selective in C-O cleavage of EG hydrogenolysis. Presently, there is very limited literature available to guide the selection of catalysts for any target product and most of the industrial catalysts are selected by expensive and time consuming screening method. This study has employed EG as a model substrate to represent the basic repeating units in macroscopic biomass molecules. Through SMSI (which promotes the formation of PdM bimetallic NPs), we have demonstrated for the first time, the possibility of fine-tuning of product specificity of biomass conversion by rationally varying electronic factors in Pd catalysts.

## 6.1 Introduction

As previously stated, the application of biomass, especially the non-food based resources, has been receiving increasing attention for relieving our dependence on non-renewable energy resources. [1-5] Poly alcohols (polyols) with repeating units of  $-\text{CH}(\text{OH})\text{CH}(\text{OH})-$  are commonly found in most biomass materials, either in the form of carbohydrates, or as the by-products in the hydrolysis of fats and oils. Based on the intense research of the past several years, significant advances have been achieved in the catalytic transformation of poly alcohol molecules into value-added chemicals or fuels. Recent work reported the production of alcohol from carbohydrate using non-fermentative approach by bacteria *Escherichia coli*. [6] However, from the industrial point of view, it is more attractive to break down large biomass molecules to fuels or commodity chemicals over inorganic based catalytic materials. This type of research presently focuses on catalytic transformation of biomass to liquid alkanes as liquid fuel through selective C-O cleavage in hydrogen. However, due to the similar homolytic cleavage energy ( $\Delta H_{\text{C-C}}$  348  $\text{kJ mol}^{-1}$  and  $\Delta H_{\text{C-O}}$  360  $\text{kJ mol}^{-1}$ ) in both C-C and C-O activation, undesirable light alkanes ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ) are also obtained. [7, 8] On the other hand, the controlled synthesis of small alcohol molecules (methanol, ethanol) through selective hydrogenolytic cleavages of C-C and C-O bonds in biomass by heterogeneous catalysis is also economically appealing, [9,10,11] as these volatile and high energy density liquids can be used as transportation fuels, also as key platform chemicals in synthesis. [3] Nevertheless, the random cleavage of C-C and C-O bonds without selectivity causes a wide distribution of the catalytic products and raises considerable separation problems. Thus, active catalysts capable of selectively cleaving C-C bond or C-O bond of the  $-\text{CH}(\text{OH})\text{CH}(\text{OH})-$  unit in hydrogen with a controlled kinetics are highly desired.

It has been demonstrated that many catalytic reactions, including hydrogenolysis of biomass molecules, require a specific strong metal and support interaction (SMSI) to give a high catalytic performance. [12] SMSI is generally attributed to the high dispersion of the noble metal on the support and the decoration of supported metal particles with reactive metallic elements derived from the support as bimetallic species. [13, 14, 15] The enhancement of catalytic properties of bimetallic nanoparticles (NPs) is assigned to the modified chemical and physical properties of the primary metal. [16, 17] In Chapter 4, the preparation of PdFe or RhFe bimetallic catalysts with tunable ratio of noble metal: Fe atoms (variable amount of Fe atoms are produced from the controllable reduction of  $\text{Fe}_2\text{O}_3$  support) has been discussed in detail. However, the successful synthesis and characterization of well-dispersed bimetallic NPs with various modifier atoms at controllable composition through the rational tuning of SMSI remains a daunting challenge. Palladium is reported to be active in the hydrogenolysis of biomass molecules and we have been able to optimize its specificity in C-C cleavage over C-O cleavage in hydrogenolysis of biomass molecules. [8, 18, 19] Also, we are interested in investigating how the electronic properties of the Pd can be modified in a wide range by various modifier atoms through the formation of bimetallic NPs. It is as well essential in establishing a fundamental relationship between the electronic structure and the catalytic activation of C-C or C-O bond of basic  $-\text{CH}(\text{OH})\text{CH}(\text{OH})-$  unit in biomass molecules.

We have obtained extremely small size (*ca.* 1-2 nm) of supported bimetallic PdM (M = Fe, Co, Ni, Zn) nanoparticles through a controlled reduction of co-precipitated powder with a narrow size distribution. The composition of the bimetallic nanoparticles can be tailored by varying the composition of the supports. Hydrogenolysis of EG is employed to probe the catalytic ability of these new supported bimetallic catalysts. EG can be produced selectively from catalytic

degradation of cellulose in hydrogen over carbide catalysts and thus it is considered as a biomass derived molecule. [20] From the perspective of molecular structure, it represents the simplest biomass derived molecule containing the  $-\text{CH}(\text{OH})\text{CH}(\text{OH})-$  unit without encountering much phase (solubility and mass transfer) issues and instability problem against rearrangement in our catalytic reactions. Thereby, hydrogenolysis of EG is considered as a model reaction to evaluate the catalytic properties of Pd-based bimetallic catalysts in catalytic biomass utilization.

## **6.2 Synthesis of the Pd-based bimetallic catalysts (PdCo, PdNi, PdZn, PdFe)**

Iron(III) oxide is chosen as the main support of Pd cluster.  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  or  $\text{Co}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were blended into the precipitation process of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  to tune the composition of the support. After the loading of palladium metal and a following pre-reduction process, a series of PdNi and PdCo bimetallic NPs with various compositions were prepared. Supported PdZn NPs were obtained after the reduction of PdO/ZnO complex which was produced by a co-precipitation method. The detailed synthesis processes were described in Chapter 3. The synthesis procedure of PdFe sample employed in this chapter is the same as that of sample 3(R=1.0) in Chapter 5.

The concentration of Co in the final Pd-based bimetallic NPs can be tuned by the amount of added cobalt precursor. The amounts of precursors added in the synthesis of supports and the calculated Co wt% are shown in Table 6-1.

**Table 6-1** The compositions of a series of cobalt blended iron oxide supports before the pre-reduction.

| Sample | Mass of added<br>Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O<br>(g) | Mass of added<br>Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O<br>(g) | Calculated<br>Co <sub>3</sub> O <sub>4</sub> ·Fe <sub>2</sub> O <sub>3</sub> | Weight % of<br>Co |
|--------|------------------------------------------------------------------------------|------------------------------------------------------------------------------|------------------------------------------------------------------------------|-------------------|
| 1      | 0.00                                                                         | 9.61                                                                         | 0.00                                                                         | 0.00              |
| 2      | 1.55                                                                         | 7.59                                                                         | 0.19                                                                         | 16.3              |
| 3      | 2.36                                                                         | 6.54                                                                         | 0.33                                                                         | 24.6              |
| 4      | 3.50                                                                         | 5.06                                                                         | 0.64                                                                         | 36.0              |
| 5      | 5.05                                                                         | 3.04                                                                         | 1.54                                                                         | 51.3              |

(Note: the calculation of Co weight % did not take the amount of Pd into account, thus the value only represents the concentration of Co in the support)

## 6.3 Characterizations of Pd-based bimetallic NPs (PdCo, PdNi, PdZn, PdFe)

### 6.3.1 Characterizations of PdCo NPs with various compositions

#### 6.3.1.1 X-ray Diffraction (XRD) and Temperature Programmed Reduction (TPR)

XRD was conducted to characterize the lattice structure of the calcined cobalt blended products. Figure 6-1a displays the XRD patterns of the samples before pre-reduction. From sample 1 (without Co) to sample 6 (without Fe), the content of blended Co(II) increases continuously. However, there is no significant change in XRD peak positions. All the diffraction patterns can be indexed to a spinel structure. It is widely known that both  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> have a spinel structure in which oxygen ions are cubic close packed (CCP) while metal cations occupy 1/2 octahedral holes and 1/8 tetrahedral holes. [21, 22] Sample 1 is Pd supported on  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> with no cobalt while sample 6 is Pd supported on Co<sub>3</sub>O<sub>4</sub> (Some Co(II) was oxidized to Co(III) during the

calcination in air). Samples 2-5 are a series of mixtures of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> with increasing Co content. Based on the amounts of precursors added, the ratios of Co<sub>3</sub>O<sub>4</sub>:Fe<sub>2</sub>O<sub>3</sub> in the supports are calculated and displayed in Table 6-1. Due to the strong overlap of the diffraction patterns, no clear phase separation of Co<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> is observed.

In order to produce bimetallic clusters, the samples are pre-reduced at 250°C. TPR (Figure 6-2) and XRD (Figure 6-1b) are employed to investigate the reduction behavior and analyze the composition of reduced catalysts. The reduction of PdO to Pd is known to readily take place at sub-ambient temperature. The two characteristic TPR peaks in sample 1 (0.0 wt% Co) as shown in Figure 6-2 are mainly attributed to the stepwise reduction of iron oxide which are taken place in two steps: Fe<sub>2</sub>O<sub>3</sub> → Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub> → Fe(0). The second step clearly takes place above 300°C corresponding to the second peak in TPR profiles, while the first peak is related to the transformation of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub>. The value of H<sub>2</sub> consumption (2.4 mmol (g cat)<sup>-1</sup>) for the first peak around 100 °C is slightly higher than the calculated theoretical value for the transformation of all the Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> (2.0 mmol (g cat)<sup>-1</sup>). This means all the Fe<sub>2</sub>O<sub>3</sub> in the support can be reduced completely to Fe<sub>3</sub>O<sub>4</sub> during the pre-reduction temperature at 250 °C. This deduction is supported by the result of XRD (Figure 6-1b). All the diffraction peaks in the pattern of reduced sample 1 can be indexed to Fe<sub>3</sub>O<sub>4</sub>. For the TPR profile of sample 6 (Pd supported on Co<sub>3</sub>O<sub>4</sub>), two broad peaks are observed, the first one before 250 °C refers to the catalytic reduction process of Co<sub>3</sub>O<sub>4</sub> to CoO while the other one after 250 °C is caused by the reduction of CoO to Co(0). The XRD pattern (Figure 6-1b) of reduced sample 6 at 250 °C reveals a typical rock salt structure, which is indexed to CoO.[23] For samples 2 to 5, the reduction processes of mixed phases (Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> and Co<sub>3</sub>O<sub>4</sub> to CoO) take place at similar temperatures, so only one peak in TPR before 250 °C is observed. However, the H<sub>2</sub> consumptions before 250 °C for all samples are

consistently greater than the theoretical value needed to reduce the mixed phases ( $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$  and  $\text{Co}_3\text{O}_4$  to  $\text{CoO}$ ) with various Co content. This suggests that accompanying this reduction process, some surface  $\text{CoO}$  must have been further converted to  $\text{Co}(0)$  with the assistance of  $\text{Pd}(0)$ . It can be understood that the reduction of  $\text{Co(II)}$  to  $\text{Co}(0)$  is more favourable than that of  $\text{Fe(II)}$  to  $\text{Fe}(0)$  resulting in the selective formation of  $\text{Co}(0)$  ( $E^0[\text{Co(II)}/\text{Co}(0)] = -0.28 \text{ V}$ ,  $E^0[\text{Fe(II)}/\text{Fe}(0)] = -0.44 \text{ V}$ ). [24, 25] With the calculated amount of  $\text{H}_2$  consumption before  $250^\circ\text{C}$  from the integration area of the peaks in TPR profiles, the quantity of produced  $\text{Co}(0)$  for each sample can be obtained. The results are presented in Table 6-2. The amount of produced  $\text{Co}(0)$  varies with the amount of added  $\text{Co(II)}$  in the synthesis procedure and reaches the peak at sample 4 (36.0 wt% Co) followed by sample 5 (51.3 wt% Co) > sample 3 (24.6 wt% Co) > sample 2 (16.3 wt% Co). The ‘volcano’ relationship is attributed to the increasing particle size of the support with the increasing Co content (as shown in Figure 6-1a the diffraction peaks of the support become narrower from sample 1 (0.0 wt% Co) to sample 6 (69.8 wt% Co)). The increase of support particle size diminishes the contact interface with Pd. Consequently, the two opposing factors of the increasing amount of added Co precursor and the increasing particle size result in a ‘volcano’ relationship between the produced  $\text{Co}(0)$  after reduction and the amount of added  $\text{Co(II)}$  in the co-precipitation process.

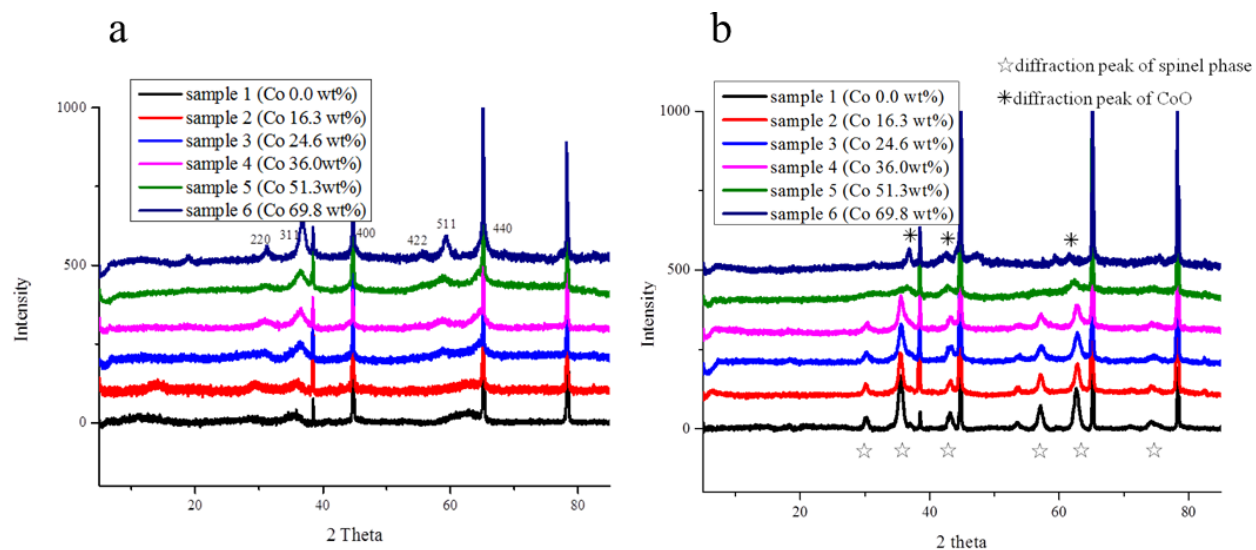


**Figure 6-1** XRD patterns of a series of Co(II) blended samples (a) before pre-reduction and (b) after reduction.

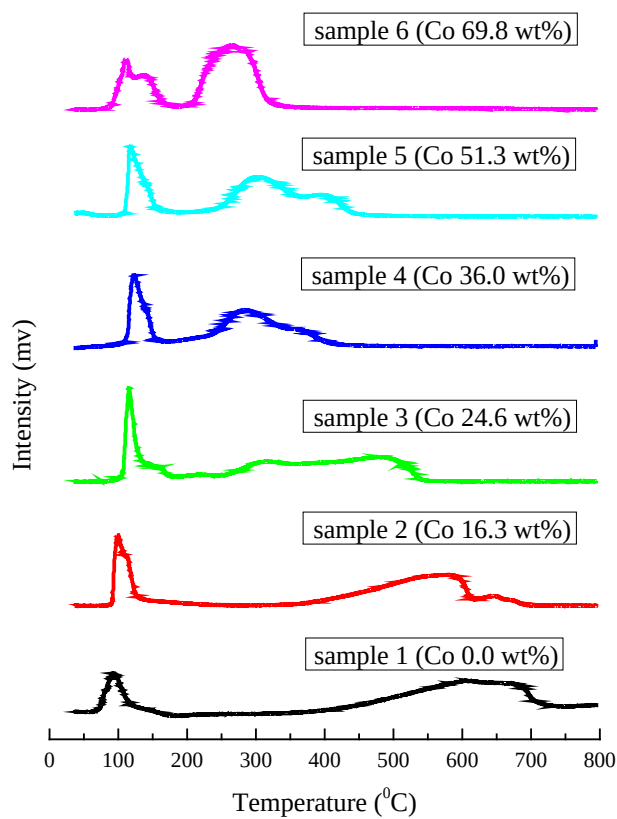


**Figure 6-2** TPR profiles for a series of cobalt blended Pd/Fe<sub>2</sub>O<sub>3</sub> samples.

**Table 6-2** The calculated quantity of Co(0) from TPR for a series of Pd/Co<sub>3</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> samples.

| Sample                                                | 2<br>(16.3wt% Co) | 3<br>(24.6wt% Co) | 4<br>(36.0 wt% Co) | 5<br>(51.3wt% Co) |
|-------------------------------------------------------|-------------------|-------------------|--------------------|-------------------|
| H <sub>2</sub> consumption<br>(mmol g <sup>-1</sup> ) | 3.9               | 5.1               | 6.0                | 6.1               |
| Produced Co<br>(mmol g <sup>-1</sup> )                | 1.6               | 2.5               | 2.9                | 2.8               |

(Note: the calculation of the amount of produced Co (0) is based on the following equation:  $N = (\text{experimental } H_2 \text{ consumption before } 250^\circ \text{C}) - (\text{theoretical } H_2 \text{ consumption of } Fe_2O_3 \text{ to } Fe_3O_4 \text{ and } Co_3O_4 \text{ to } CoO).$ )

### 6.3.1.2 X-ray Photoelectron Spectroscopy (XPS)

Figure 6-3 displays the XPS curves of cobalt and iron for reduced sample 2 (16.3 wt% Co). Two groups of peaks are observed in the spectroscopy of Co (Figure 6-3a). The one located around 780 eV is assigned to the 2p<sub>3/2</sub> peak of Co accompanied by its satellite peak (786 eV), the other one at 795 eV corresponds to 2p<sub>1/2</sub> peak of Co which is also followed by a satellite peak (803 eV).[26] The 2p<sub>3/2</sub> peak of Co can be evidently fitted into 2 peaks. One is located at 780.4 eV corresponding to the signal of Co(II) while the other one is around 777.8 eV which can be clearly assigned to the signal of Co(0).[27] The intense peak at 777.8 eV indicates a significant proportion of Co(0) in the catalyst. Whereas from the curve of Fe (Figure 6-3b), a binding energy of 710.2 eV is observed. This value is consistent with the literature value of Fe<sub>3</sub>O<sub>4</sub> indicating the preferential H<sub>2</sub> reduction of Co(II) to Co(0) which has a less negative reduction potential than Fe(II) to Fe(0).[28]

The XPS curves of cobalt for a series of reduced samples are displayed in Figure 6-4. With increasing content of Co(II), various amount of Co(0) atoms are produced in the reduction process. And the corresponding Co(0) 2p<sub>3/2</sub> signal grows until it peaks at sample 4. This is consistent with the TPR results. The change of XPS signal of Co(0) indicates the successful

control of Co concentration in the active site of the catalysts.

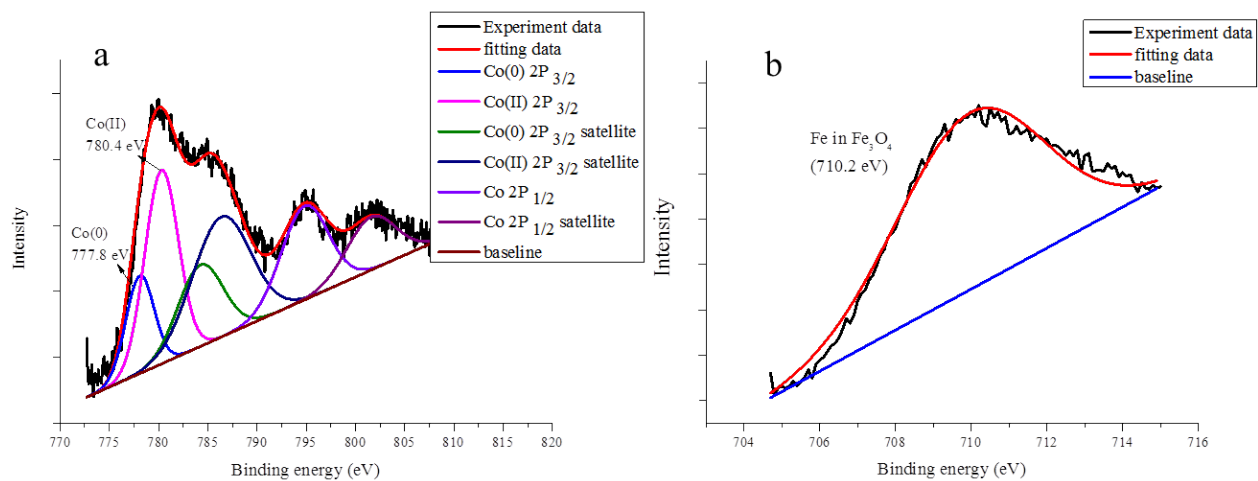


**Figure 6-3** XPS curves and the corresponding fitting results of (a) Co and (b) Fe in the reduced sample 2 (16.3 wt% Co).

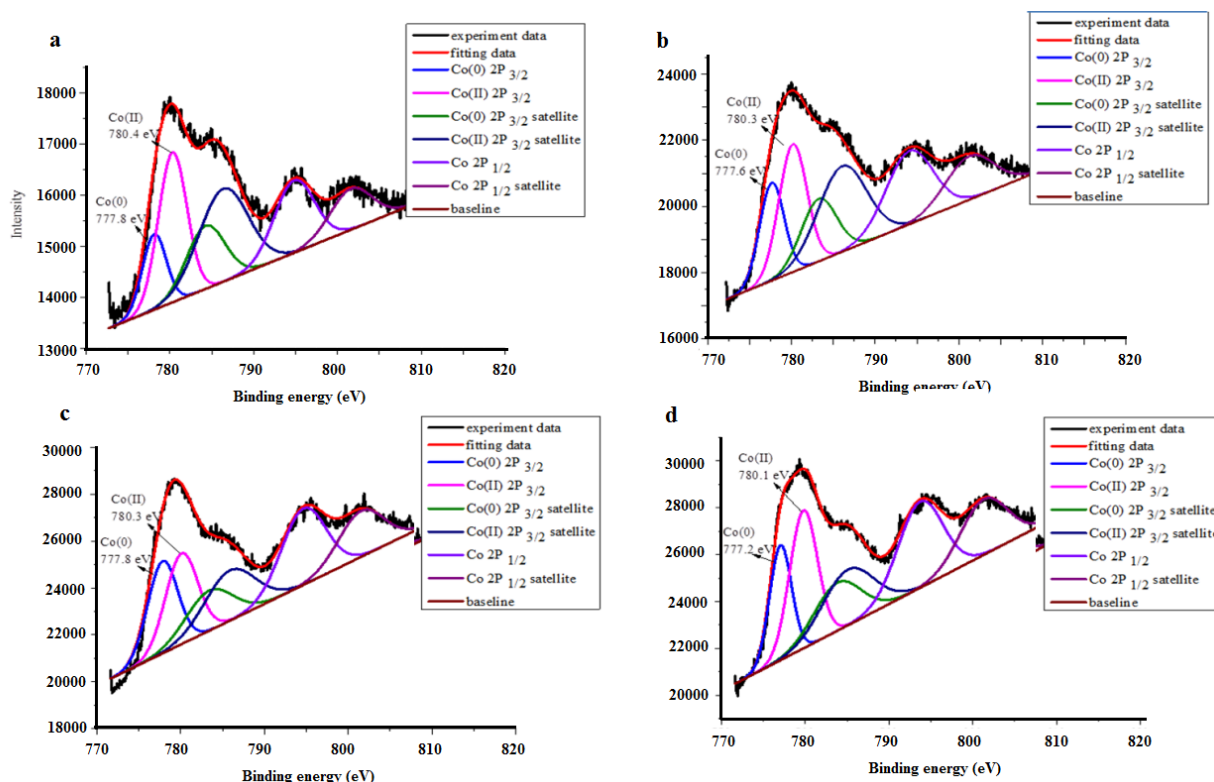


**Figure 6-4** XPS curves of Co in (a) sample 2 (16.3 wt% Co); (b) sample 3 (24.6 wt% Co); (c) sample 4 (36.0 wt% Co); (d) sample 5 (51.3 wt% Co) after the pre-reduction.

### 6.3.1.3 Extended X-ray Absorption Fine Structure (EXAFS)

The EXAFS results of the Pd samples with variable content of cobalt in the iron oxide support are displayed in Figure 6-5 and Table 6-3. It is noted the low but slightly increasing total coordination number (CN) (from 6.8 to 7.9) with an increasing Co content. We have estimated the average size of Pd containing NPs to be 1.5-2.0 nm from the analysis of the total CN within acceptable R- and D-W factors. [29] Another feature that has been noted in EXAFS is the direct observation of a Pd–Co distance (number of neighbour Co ranges from 2.0 to 4.7) at 2.57 Å besides the distorted Pd–Pd distance at 2.70 Å after reduction (sample kept in inert atmosphere). This confirms the formation of surface ‘PdCo’ bimetallic NPs of various compositions but with

virtually the same particle size. As shown in Figure 6-5a, the number of first shell Co around each Pd atom decreases in the order of sample 4 (36.1 wt% Co) > sample 5 (51.3 wt% Co) > sample 3 (24.6 wt% Co) > sample 2 (16.3 wt% Co). The EXAFS result reflects the fact that the composition of the PdCo bimetallic NPs can be tuned by varying the composition of the supports, which agrees with the TPR result (Figure 6-2, Table 6-2).

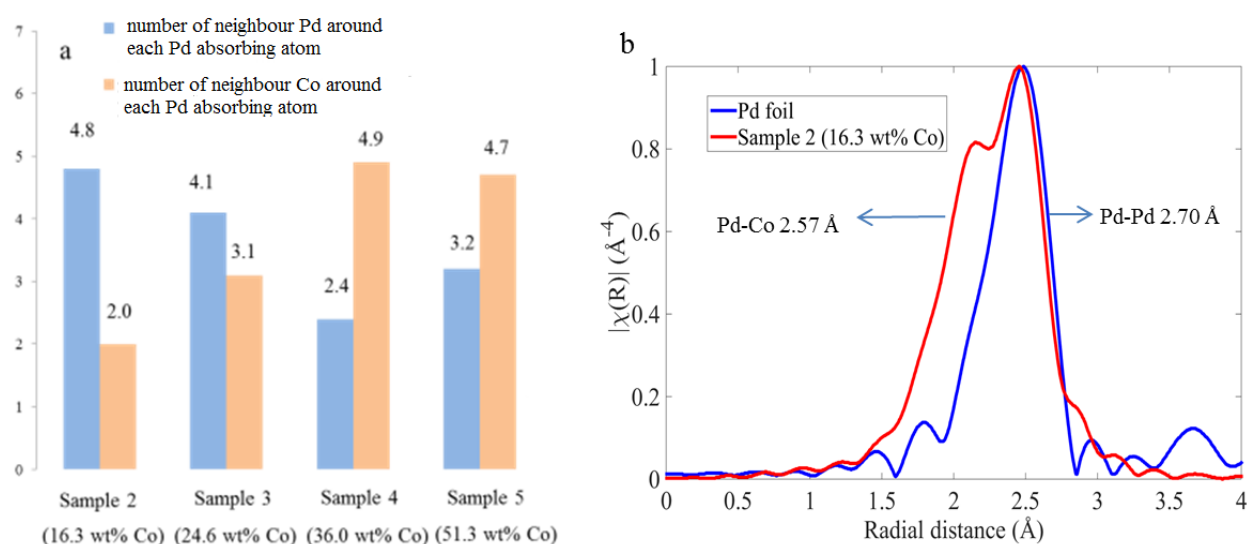


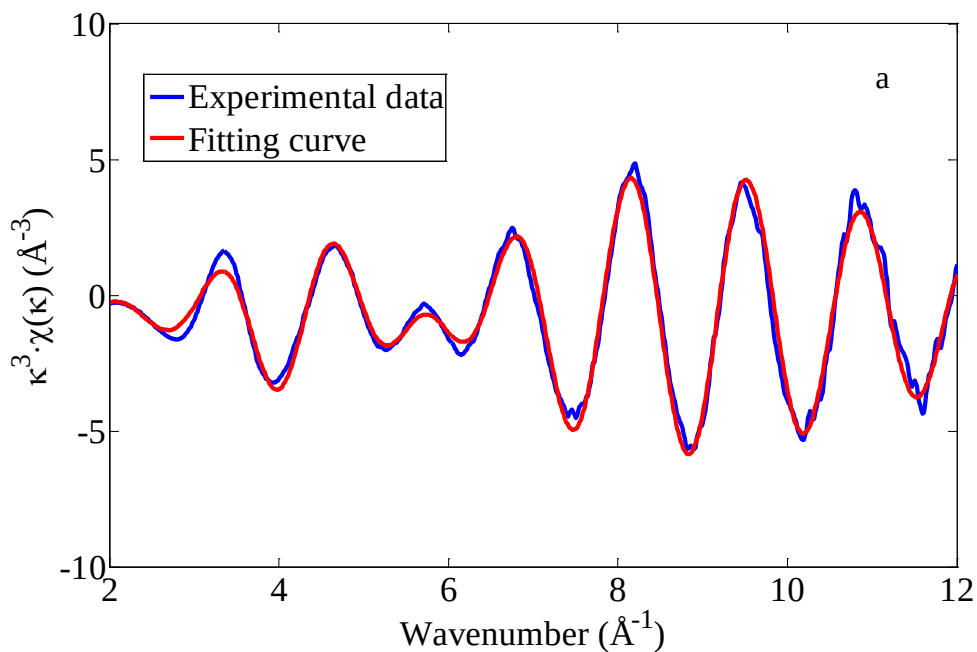
**Figure 6-5** (a) Number of neighbour Pd (NPd) and Co atoms (NCo) around each Pd absorbing atom derived from EXAFS fittings; (b) the Fourier transform of the EXAFS curves (typical EXAFS curves against radial distance) for sample 2 (16.3 wt% Co) with a reference of Pd foil.

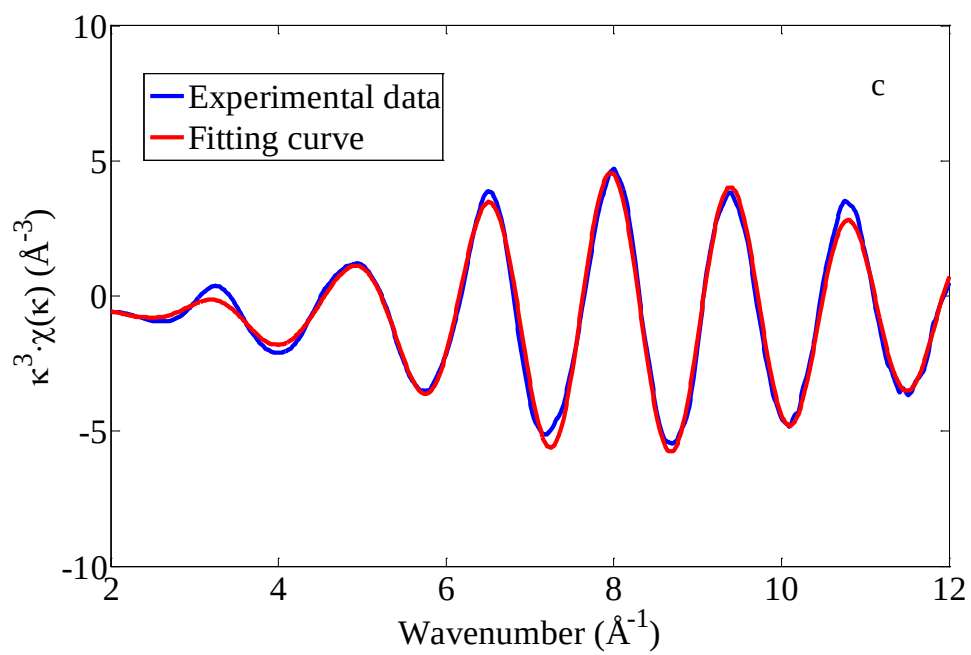
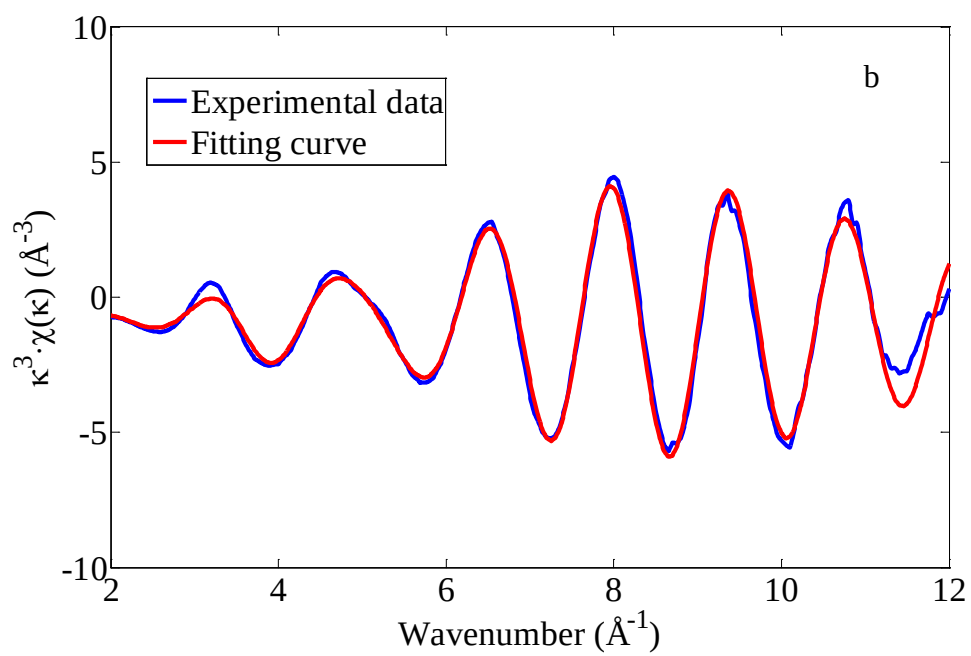
**Table 6-3** Average coordination environment of a Pd atom from EXAFS of a series of PdCo samples.

| Sample | Total CN | $\Delta E$ (eV) | Pd-Pd<br>distance (Å) | D-W<br>factor(Å <sup>2</sup> ) | Pd-Co<br>distance (Å) | D-W<br>factor(Å <sup>2</sup> ) | R-factor |
|--------|----------|-----------------|-----------------------|--------------------------------|-----------------------|--------------------------------|----------|
| 2      | 6.8(4)   | 1.2             | 2.69(1)               | 0.010(1)                       | 2.58(1)               | 0.010(1)                       | 0.4%     |
| 3      | 7.2(7)   | -2.2            | 2.70(1)               | 0.013(2)                       | 2.57(1)               | 0.005(1)                       | 0.8%     |
| 4      | 7.3(7)   | -3.8            | 2.71(1).              | 0.010(1)                       | 2.55(1)               | 0.006(1)                       | 0.6%     |
| 5      | 7.9(5)   | -3.6            | 2.70(1)               | 0.008(1)                       | 2.58(1)               | 0.012(1)                       | 0.4%     |

(“CN” is coordination number; “ $\Delta E$ ” is the energy difference between the experimental absorption energy and the calculated value in curve fitting; “D-W” is Debye Waller; “R factor” is the indication of the quality of curve fitting)

The corresponding fitting curves of Pd in  $k^3$  space for a series of reduced PdCo samples are shown in Figure 6-6. The experimental curves and the fitting results match well with each other indicating the reliability of the derived data.





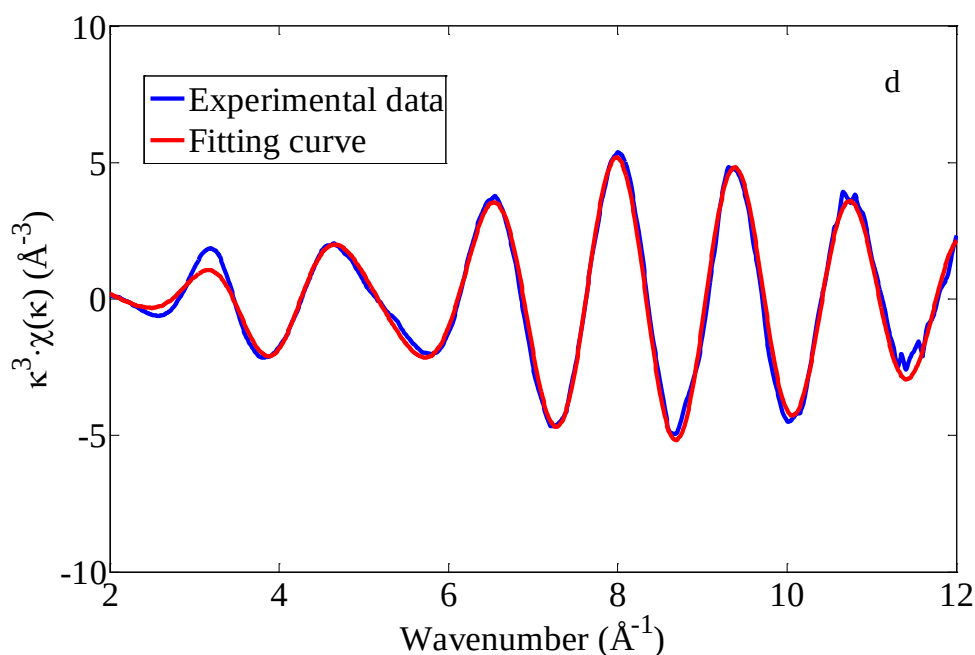
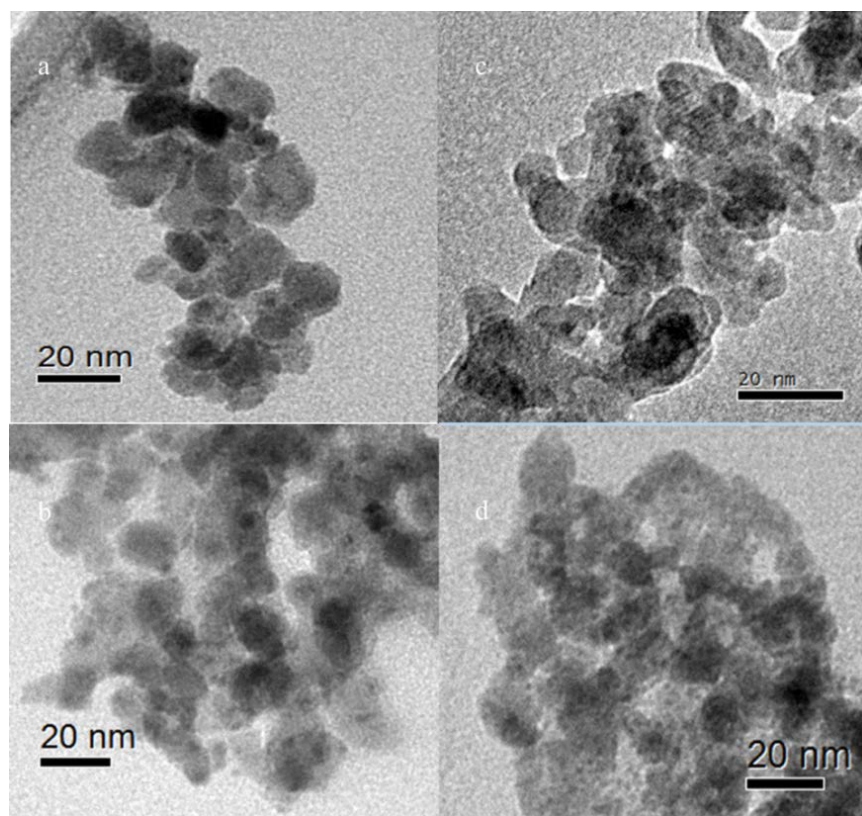


**Figure 6-6**  $k^3$  space EXAFS curves of Pd in an R range of 2-12 for a series of reduced PdCo samples: (a) sample 2 (16.3 wt% Co), (b) sample 3 (24.6 wt% Co), (c) sample 4 (36.0 wt% Co), (d) sample 5 (51.3 wt% Co). (blue: experiment data; red: fitting data)

#### 6.3.1.4 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) has been conducted to acquire the detailed microscopic view for the PdCo particles and the results are displayed in Figure 6-7. In these samples, a large number of small bimetallic particles are observed to be dispersed on the support. The size ranges from *ca.* 0.8 to 2.4 nm in diameter, with 1.5 nm being the predominant particle size, consistent with the estimation from the EXAFS results. It also suggests that the amount of blended Co(II) does not influence the particle size significantly.



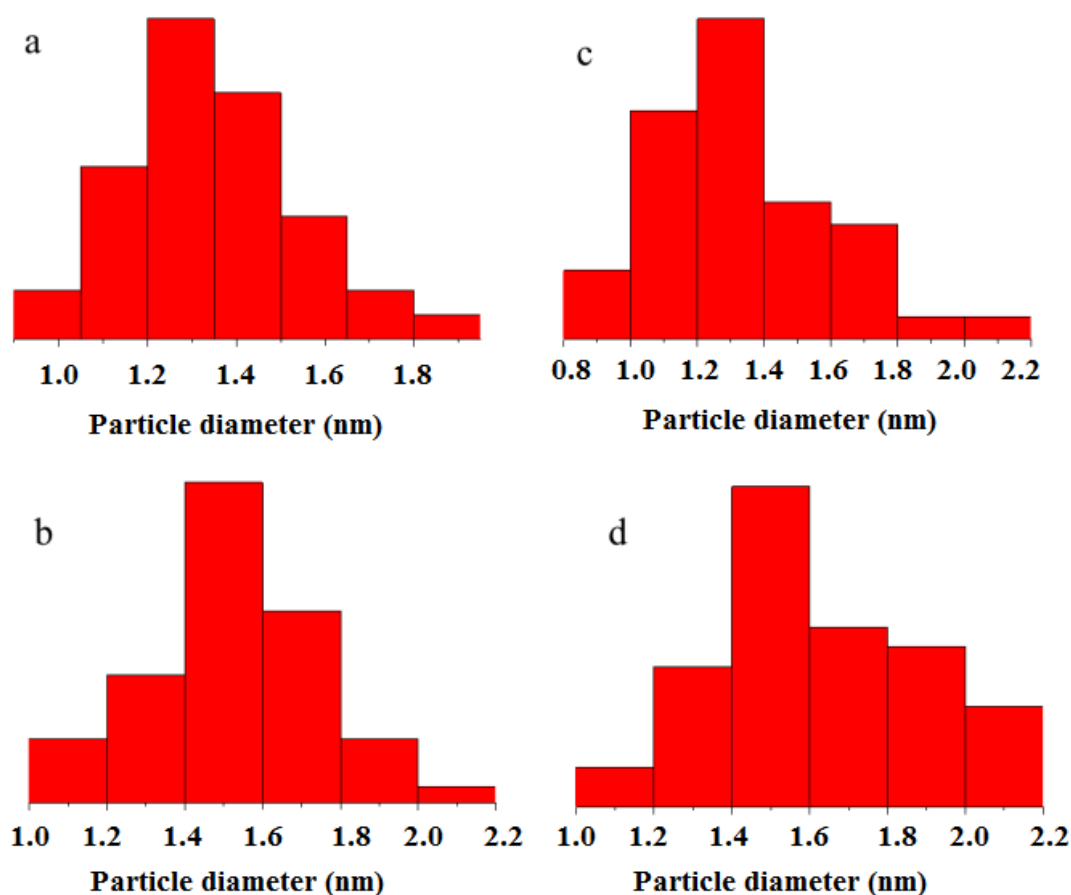


**Figure 6-7** (Top) TEM images of reduced (a) sample 2 (16.3 wt% Co), (b) sample 3 (24.6 wt% Co), (c) sample 4 (36.0 wt% Co), (d) sample 5 (51.3 wt% Co). (Bottom) Pd particle size distribution in (a) sample 2(16.3 wt% Co), (b) sample 3(24.6 wt% Co), (c) sample 4 (36.0 wt% Co), (d) sample 5 (51.3 wt% Co).

### 6.3.2 Characterization of PdM (M=Fe, Co, Ni, Zn) nanoparticles

A series of PdM (M=Fe, Co, Ni, Zn) bimetallic NPs with comparable composition were also synthesized to investigate the modification mechanism of modifier atoms on the properties of Pd. The coordination environments of Pd in the bimetallic NPs, derived from EXAFS at the Pd K edge, are summarized in Figure 6-8 and Table 6-4. The secondary atom M (M = Fe, Co, Ni, Zn) is indeed observed in the first scattering shell of the absorbing Pd, confirming the formation of

PdM bimetallic NPs and the existence of SMSI in all the samples. Also, the total coordination numbers of each absorbing Pd atom are within the range of 6-7, indicative of similar particle sizes for the various Pd-based bimetallic NPs. In addition, the number of neighbour M (M = Fe, Co, Zn) around each Pd atom is controlled to be around 2 which indicates the comparable ratio of Pd to modifier atoms in the bimetallic particles.

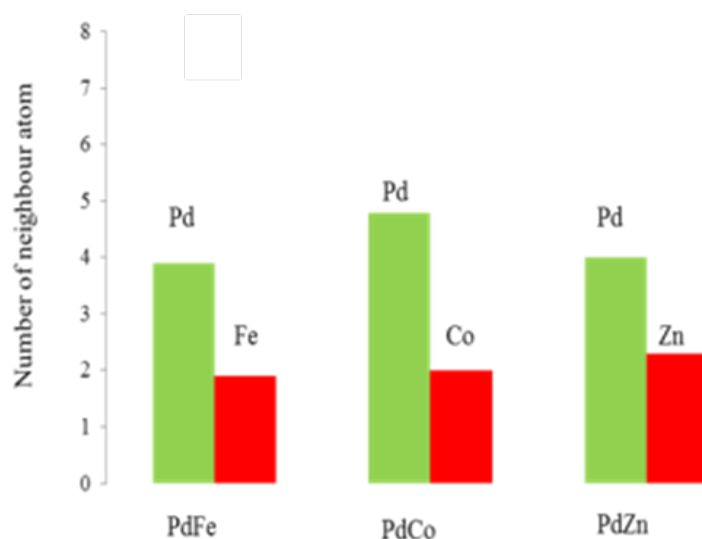


**Figure 6-8** The number of neighbour Pd (NPd) and secondary atom M (NM, M = Fe, Co, Zn) around each Pd absorbing atom in the PdFe, PdCo and PdZn bimetallic NPs. (For PdNi, NNi = 6.3 NPd=0, which indicates the much higher concentration of Ni than that of Fe, Co, Zn in the PdM NPs.)

**Table 6-4(a)** Total coordination number of a Pd absorbing atom, R factor and  $\Delta E$  value of each fitting in PdFe, PdCo, PdNi and PdZn clusters.

| Sample | Total CN | R factor | $\Delta E$ (eV) |
|--------|----------|----------|-----------------|
| PdFe   | 5.8(6)   | 2.7%     | -0.8            |
| PdCo   | 6.8(4)   | 0.4%     | 1.2             |
| PdNi   | 6.3(5)   | 1.1%     | -7.8            |
| PdZn   | 6.3(7)   | 2.4%     | -5.0            |

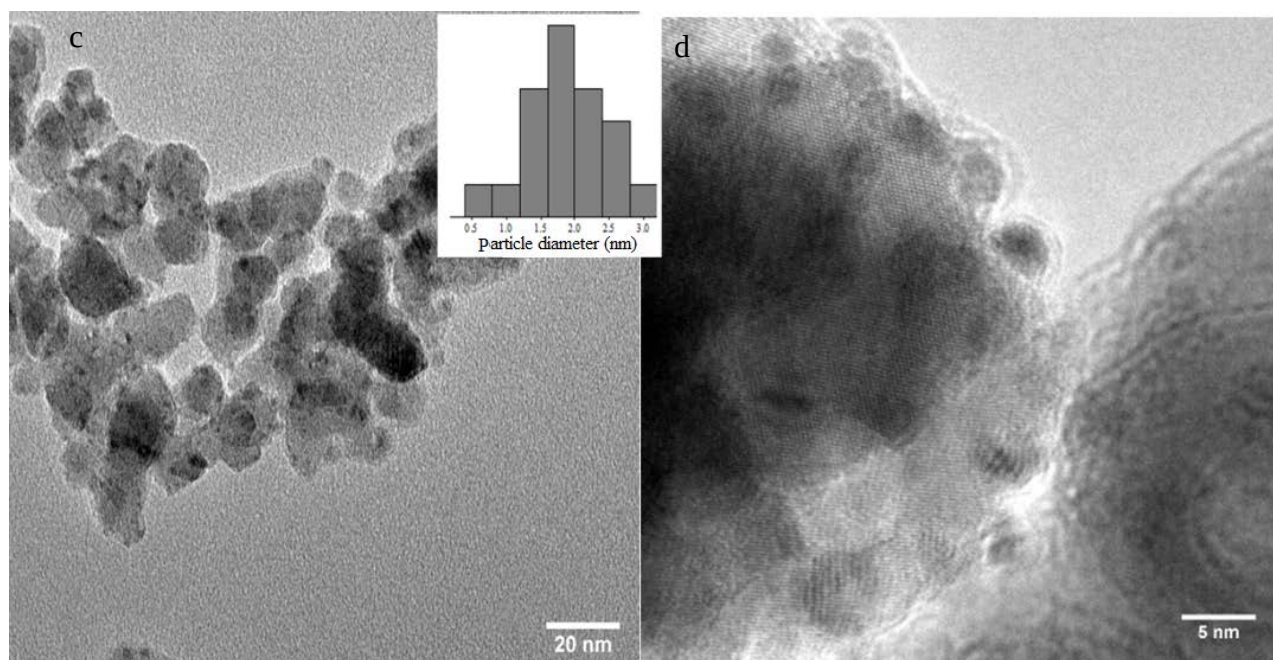
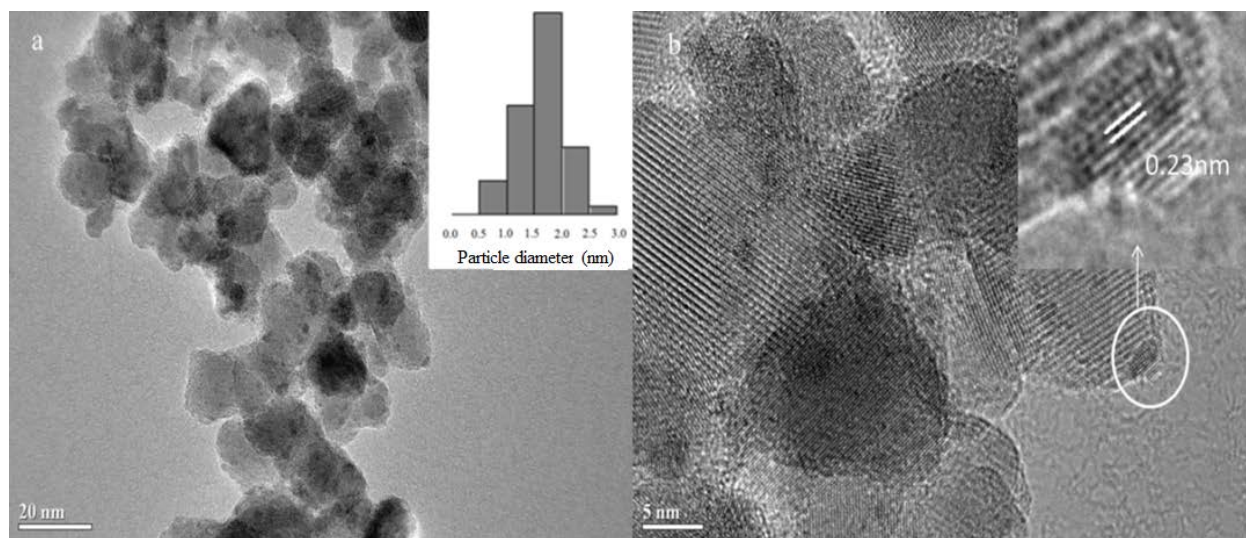
**Table 6-4(b).** Average coordination environment of a Pd absorbing atom for the PdFe, PdCo, PdNi, PdZn from the EXAFS result.

| Sample      | Scatting pair | Bond length (Å) | CN     | D-W factor(Å <sup>2</sup> ) |
|-------------|---------------|-----------------|--------|-----------------------------|
| <b>PdFe</b> | Pd-Pd         | 2.69(1)         | 3.9(4) | 0.011(1)                    |
|             | Pd-Fe         | 2.57(1)         | 1.9(2) | 0.010(1)                    |
| <b>PdCo</b> | Pd-Pd         | 2.69(1)         | 4.8(2) | 0.010(1)                    |
|             | Pd-Co         | 2.58(1)         | 2.0(2) | 0.010(1)                    |
| <b>PdZn</b> | Pd-Pd         | 2.70(1)         | 4.0(5) | 0.012(1)                    |
|             | Pd-Zn         | 2.56(1)         | 2.3(2) | 0.004(2)                    |
| <b>PdNi</b> | Pd-Pd         | N.A.            | 0.0    | N.A.                        |
|             | Pd-Ni         | 2.56(1)         | 6.3(5) | 0.007(1)                    |

(“CN” is coordination number; “ $\Delta E$ ” is the energy difference between the experimental absorption energy and the calculated value in curve fitting; “D-W” is Debye Waller; “R factor” is the indication of the quality of curve fitting; N.A. is the abbreviation not applicable)

As shown in Table 6-4a, all the R factors for EXAFS fittings are below 3% indicating the reliability of the results. In the PdNi sample, no Pd-Pd scattering path is observed which implies the much higher concentration of Ni in the bimetallic phase than that of the other transition metal in PdM. The failure of controllable synthesis of PdNi for the systematic comparison among PdM alloys is presumably due to the fast reduction process of Ni(II) to Ni(0).

Typical TEM images of supported PdM (M=Fe, Co, Zn, Ni) are shown in Figure 6-9; a clear lattice fringe of 0.23 nm is observed on the surface of the sample (Figure 6-9b) which should be assigned to the (111) plane of Pd-based particle. [30] The particle size in all the samples ranged from *ca.* 0.5 to 2.5 nm in diameter, with particles of 1.0 to 2.0 nm being the most commonly measured size. This is consistent with the results of EXAFS and indicative of the similar particle size among the PdM particles.



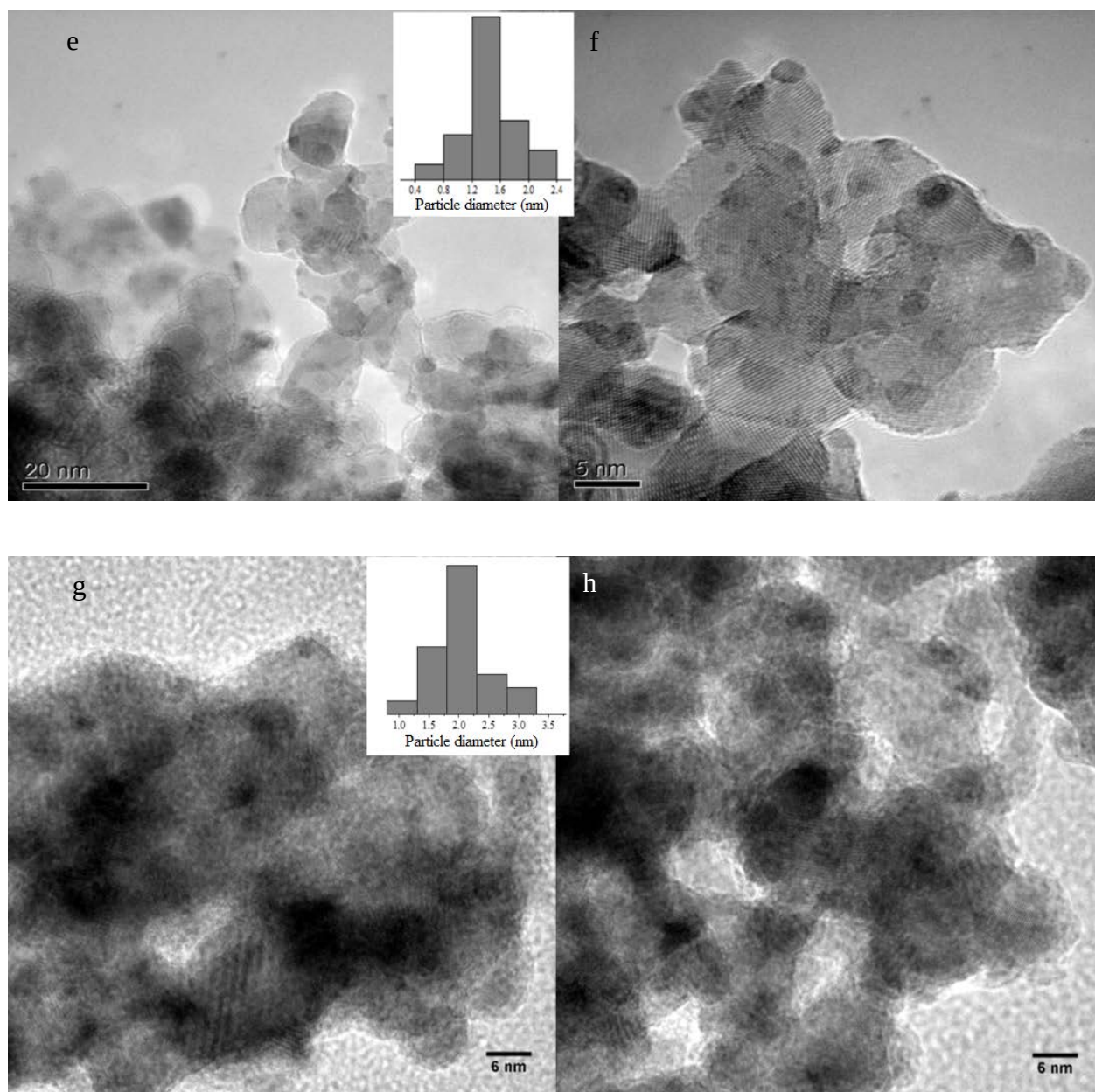


**Figure 6-9** TEM and HRTEM of supported (a, b) PdFe, (c, d) PdCo, (e, f) PdZn particles with NM around 2(M=Fe, Co, Zn) and (g, h) PdNi with NNi=6.3.

## 6.4 Catalysis and modeling computation

### 6.4.1 Catalysis procedure

Aqueous hydrogenolysis of EG in hydrogen over these Pd-based supported bimetallic catalysts is used as a model reaction to investigate their catalytic performance in biomass utilization. The detailed catalytic tests procedure was described in Chapter 3. The conversion, product selectivity and the value of “Selective C-C cleavage: Selective C-O cleavage” are calculated as following:

$$\text{Conversion} = \frac{\text{moles of EG before reaction} - \text{moles of EG after reaction}}{\text{moles of EG before reaction}}$$

$$\text{Selectivity} = \frac{\text{moles of specific product} * \text{its mole carbon number}}{\sum \text{moles of each product} * \text{its mole carbon number}}$$

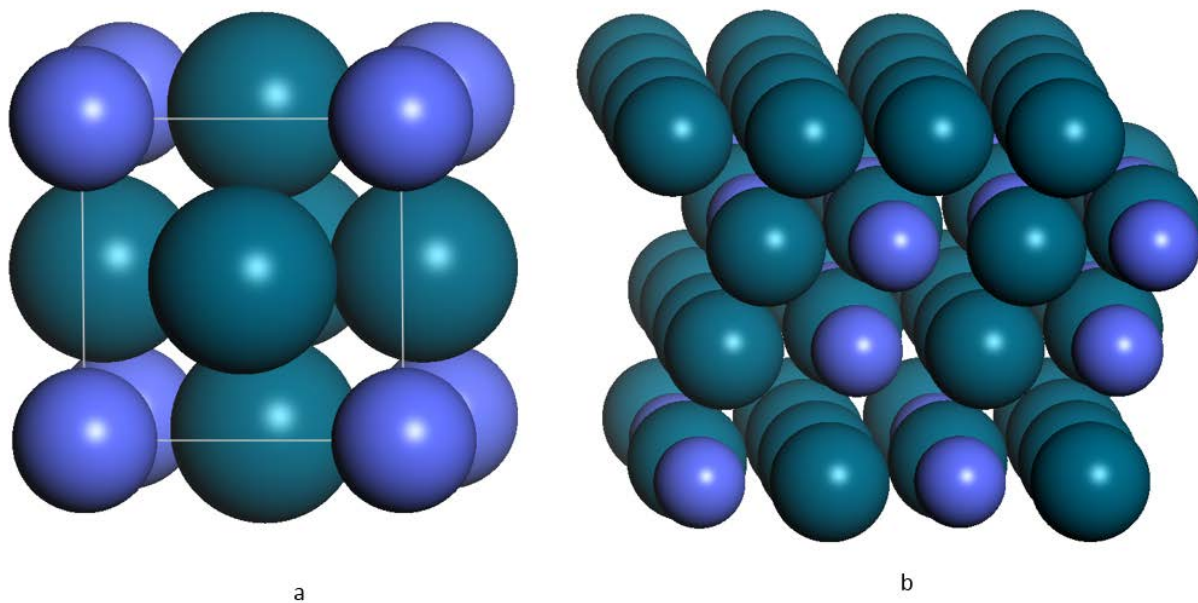
$$\frac{\text{selective C - C cleavage}}{\text{selective C - O cleavage}} = \frac{\text{moles of EG consumed to produce the obtained methanol}}{\text{moles of EG consumed to produce the obtained ethanol}}$$

### 6.4.2 DFT Computation methods

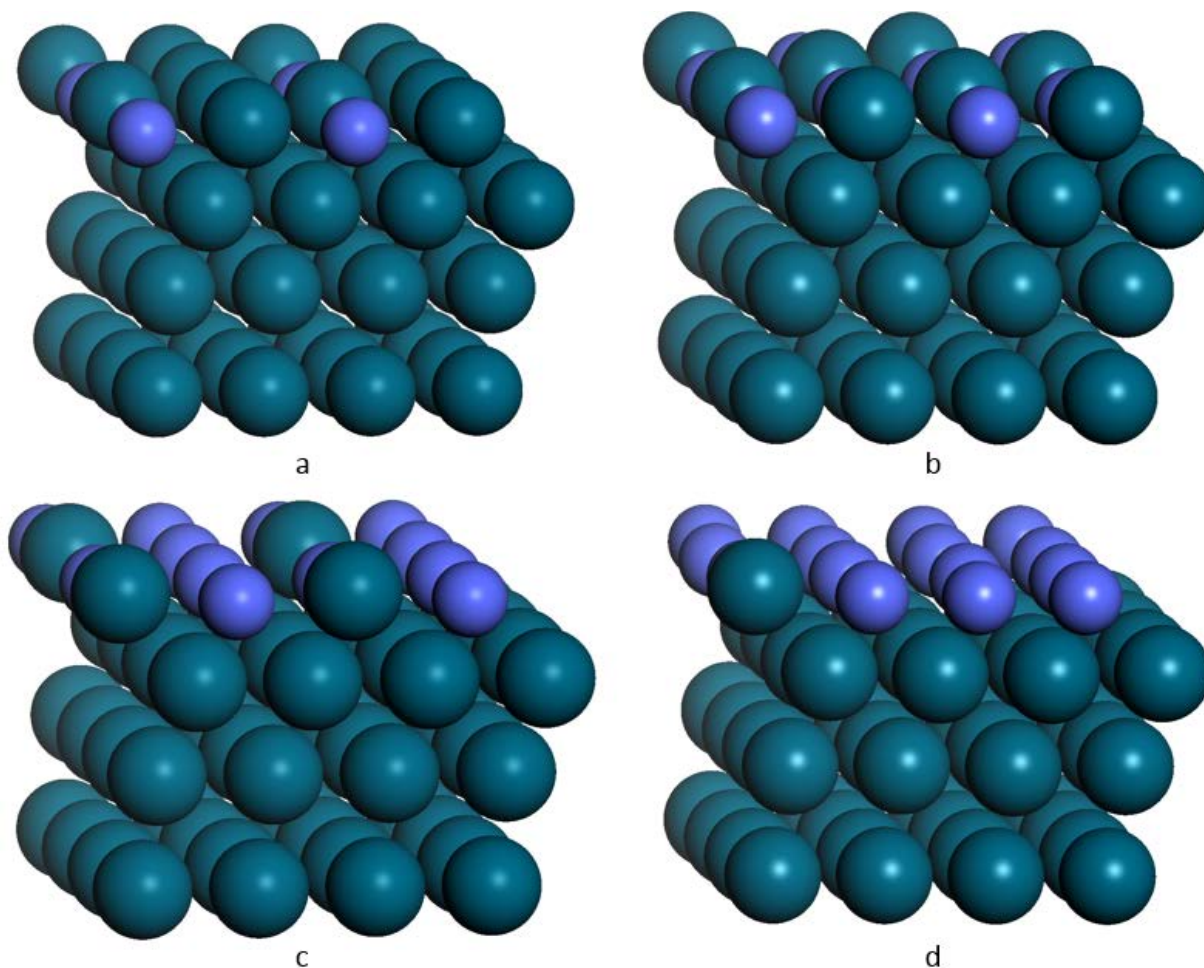
The DFT calculations were finished with collaboration of Dr. Jin Qu from our group. All calculations were performed in the framework of DFT by using the Vienna ab initio simulation package (VASP 4.6). [31-34] The projector-augmented wave (PAW) potentials were used for the core electron interaction. [35, 36] The Perdew–Burke–Ernzerhof (PBE) functional based on the generalized gradient approximation (GGA) was employed to evaluate the non-local exchange-correlation energy. [37, 38] A plane wave basis set with a cutoff energy of 400 eV was used. For structure optimization, the ionic positions were allowed to relax until the forces were less than 0.05 eV/Å. Spin polarization is included for all the calculations.

As showed in Scheme 6-1,  $\text{Pd}_3\text{M}$  ( $\text{M}=\text{Fe}, \text{Co}, \text{Zn}$ ) anti-segregation bulk alloy models are conducted to investigate the effect of secondary element on Pd which are similar to previous studies. [39-46] In these models, the Pd atoms occupy the face-centered positions while the M metal atoms replace the corners so the ratio of Pd: M is 3:1 in the unit cell. A 3:1 ratio of Pd: M is set as it corresponds to a 2:1 number ratio of neighbour Pd: neighbour M around each Pd absorbing atom. This matches with the experimental composition of PdM bimetallic NPs ( $\text{NPd}=4, \text{NM}=2, \text{M}=\text{Fe}, \text{Co}, \text{Ni}$ ). The k-point grid determined by the Monkhorst-Pack method was  $16\times 16\times 16$ . The most abundant close-packed  $\text{Pd}_3\text{M}(111)$  surface was modeled by a periodic slab model with four layers of metals. The alloy atoms in the top layer were exchanged to the second layer. A  $4\times 4$  surface unit cell was used and the bottom layer was fixed during all geometry optimizations. A vacuum layer of 15 Å along the z direction perpendicular to the surface (the x and y directions being parallel to the surface) was employed to prevent spurious interactions between the repeated slabs.

To study the concentration effects of Co modification, a simple model of non-segregated surface alloy was used here (the composition of PdM bulk alloy model cannot be set freely due to the consideration of symmetry for the calculation although it can reflect the structure of alloy better than this simple surface substitution model). Various amounts of Co as impurity were induced to substitute for surface Pd atoms on Pd(111) as showed in Scheme 6-2. The k-point grid determined by the Monkhorst-Pack method was  $5\times 5\times 1$ .



**Scheme 6-1** (a) Pd<sub>3</sub>M bulk alloy model and (b) close packed (111) surface model (Blue balls represent Pd atoms and purple balls are secondary atoms (Fe, Co, Zn)).



**Scheme 6-2** Surface alloy models of (a)Pd<sub>3</sub>Co; (b)PdCo; (c)PdCo<sub>3</sub>; (d) PdCo<sub>15</sub> (blue balls represent Pd atoms and purple balls are Co atoms, the structure of Pd<sub>15</sub>Co is the same with Scheme 6-2d but only shows opposite position of Pd and Co on the surface layer).

### 6.4.3 Results of Catalytic tests and modeling computation

The catalysis results of PdM (M = Fe, Co, Zn) NPs (with comparable amount of modifier atom in the bimetallic phase) in the hydrogenolysis of EG are shown in Table 6-5. There are 4 major primary products (CH<sub>4</sub>, CO<sub>2</sub>, CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH) detected. As stated in Chapter 5, the catalytic cleavage of C-O in hydrogen produces C<sub>2</sub>H<sub>5</sub>OH whilst the C-C cleavage produces CH<sub>3</sub>OH. CH<sub>4</sub> and CO<sub>2</sub> are produced by the breakage of all the bonds in EG followed by

extensive hydrogenation reaction or steam reforming, respectively.[9] The activities of selective C-C and C-O bond rupture of the substrate molecule are reflected straightforward by the CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH selectivity. As shown in Table 6-5, the corresponding methanol selectivity decreases significantly from 50.1% for PdFe to 18.6% for PdZn, while the ethanol selectivity increases accordingly from 3.0% to 23.6%. The mole ratios of “selective cleavage of C-O: selective cleavage of C-C” are also calculated from the mole ratios of ethanol to methanol. For PdFe, the value is 0.06 which reveals the extremely high selectivity for C-C cleavage over C-O cleavage (selectivity of C-C cleavage reaches 95%). Thereby, methanol is produced as the dominant liquid product. Among the PdM bimetallic NPs, the catalytic ability of selective C-O cleavage over C-C cleavage is enhanced in the following order: PdFe < PdCo < PdZn. The catalytic performances allude to the different influences of modifier atoms on the catalytic properties of Pd. The catalytic result of PdNi is presented separately in Table 6-6 due to the much higher Ni concentration than that of Fe, Co, Zn in the Pd-based bimetallic phase.

**Table 6-5** Catalytic performance of PdFe, PdCo and PdZn bimetallic NPs in hydrogenolysis of EG (0.50 g catalyst; 30 mL of EG (5 wt%); 50 bar H<sub>2</sub> (r.t.); 250 °C for 24 h).

| Active site | Conv. % | Select. % CH <sub>3</sub> OH | Select. % C <sub>2</sub> H <sub>5</sub> OH | Select. % CO <sub>2</sub> | Select. % CH <sub>4</sub> | Selective cleavage of C-O:C-C |
|-------------|---------|------------------------------|--------------------------------------------|---------------------------|---------------------------|-------------------------------|
| PdFe        | 25.0    | 50.1                         | 3.0                                        | 45.1                      | 1.2                       | 0.06                          |
| PdCo        | 31.2    | 35.9                         | 12.7                                       | 30.9                      | 18.7                      | 0.36                          |
| PdZn        | 4.6     | 18.6                         | 23.6                                       | 56.8                      | 0.4                       | 1.27                          |

*(conv. and select. are abbreviations of conversion and selectivity, respectively)*

**Table 6-6** Catalytic performance of supported PdNi sample in the hydrogenolysis of EG (0.50 g catalyst; 30 mL of EG (5 wt%); 50 bar H<sub>2</sub> (r.t.); temp. = 250 °C for 24 h).

| Active site | Conv.<br>% | Select. %<br>CH <sub>3</sub> OH | Select. %<br>C <sub>2</sub> H <sub>5</sub> OH | Select. %<br>CO <sub>2</sub> | Select. %<br>CH <sub>4</sub> | Selective cleave of<br>C-O:C-C |
|-------------|------------|---------------------------------|-----------------------------------------------|------------------------------|------------------------------|--------------------------------|
| PdNi        | 54.8       | 12.7                            | 12.8                                          | 1.5                          | 73.0                         | 1.01                           |

(conv. and select. are abbreviations of conversion and selectivity, respectively)

The calculated *d*-band structure of the PdM bimetallic NPs are shown in Figure 6-10a. The *d*-band filling of homogenous 3:1 alloys indeed shows an increasing trend across the periodic elements with an increasing number of *d*-orbital electron. On the other hand, the resulting surface *d*-band center positions of Pd<sub>3</sub>M for the four transition metals are being uplifted accordingly as PdFe  $\approx$  PdCo < PdNi < PdZn. This is governed presumably by the dominant effect of an increasing electron filling, despite the fact that the 3*d* energy levels for the transition metals should be gradually decreasing due to increasing effective nuclear charge ( $Z_{eff}$ ) across the period (*d*-band contraction). Note that Pd<sub>3</sub>Fe and Pd<sub>3</sub>Co have similar *d*-band center positions due to the contributions from two opposing factors: the uplift by increased electron filling and the downshift due to *d*-band contraction. The significant change either in electron filling or *d*-band center position could dominate the final product distribution of the catalytic hydrogenolysis reaction of EG. Figure 6-10b shows a plot of “selective cleavage of C-O: selective cleavage of C-C” versus the calculated *d*-band filling of the three transition metals (M) blended Pd<sub>3</sub>M alloys (M= Fe, Co, Ni), together with the values from PdNi. Since the calculated *d*-band filling value of PdNi alloys remains constant at 0.88 for a wide range of Ni content as shown in Table 6-8, the catalytic results of PdNi can be compared with other PdM catalyst, despite the much higher

concentration of Ni ( $\text{NNi}=6.3$ ) than those of the other modifier metals. From Figure 6-10b, the increasing ability of the catalysts to carry out C-O bond cleavage over C-C bond cleavage guided by increasing  $d$ -band filling of PdM from PdFe, PdCo, PdNi to PdZn is very apparent. On the other hand, the selective bond cleavage may also be affected by the uplifted  $d$ -band center positions of the alloys. According to Figure 6-10b, the  $d$ -band positions of Pd<sub>3</sub>Fe and Pd<sub>3</sub>Co are close to each other, while Pd<sub>3</sub>Zn and Pd<sub>3</sub>Ni show higher values. Coincidentally, the values of “selective cleavage of C-O: selective cleavage of C-C” for PdZn and PdNi catalysts show a more positive deviation from the projected linear line of  $d$ -band filling effect over PdFe and PdCo alloys. This may reflect the enhancement effect of high  $d$ -band center position on C-O cleavage.

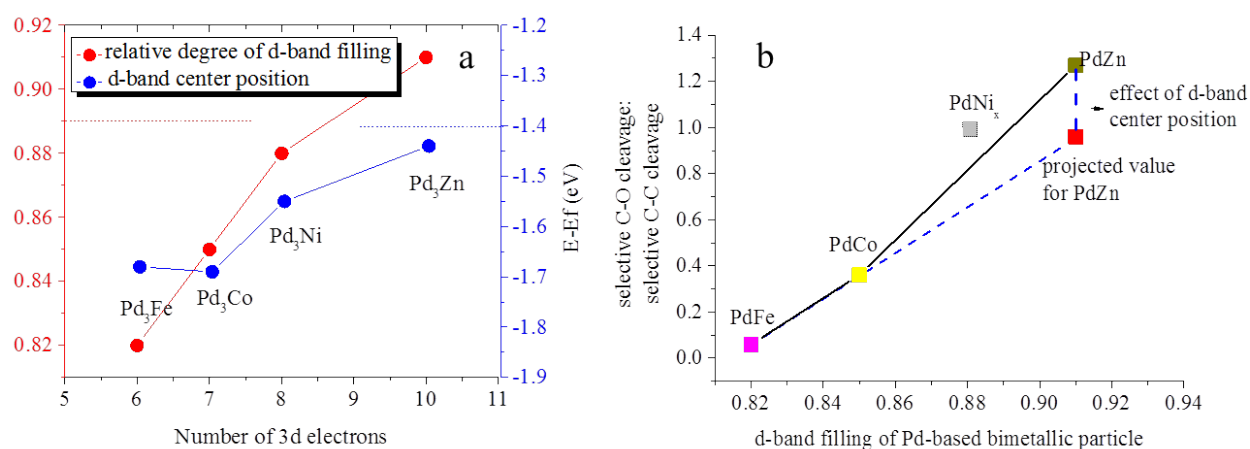


**Figure 6-10** (a) Calculated  $d$ -band filling and  $d$ -band center position of Pd<sub>3</sub>M (M = Fe, Co, Ni, Zn) (the corresponding values of Pd are labelled in the figure as dash lines); (b) The effect of  $d$ -band filling and  $d$ -band center position of Pd<sub>3</sub>M bimetallic nanoparticles (M = Fe, Co, Zn) on selective C-O:C-C cleavage.

The corresponding calculated surface density of states (SDOS) diagrams for the Pd<sub>3</sub>M alloys are shown in Figure 6-11.

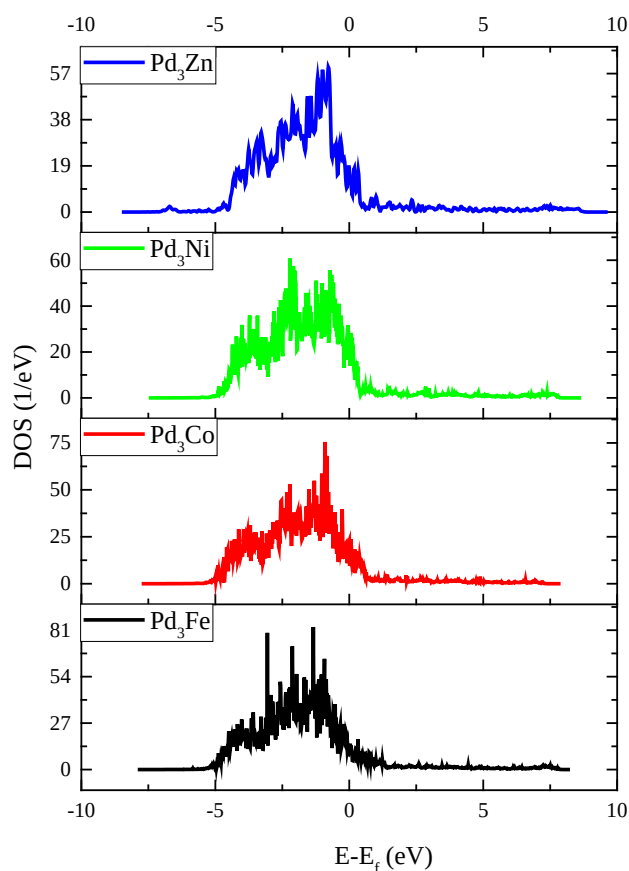


**Figure 6-11** Calculated surface density of states (DOS) diagrams of PdFe, PdCo, PdNi, PdZn.

The lattice parameters of the Pd<sub>3</sub>M (M=Fe, Co, Zn) alloy models were obtained after a bulk optimization. As shown in Table 6-7, the value of Pd<sub>3</sub>Zn alloy is higher than those of Pd<sub>3</sub>Co and Pd<sub>3</sub>Fe which is consistent with the result of EXAFS shown in Table 6-4b (the distance of Pd-Pd in PdZn is longer than those in PdFe and PdCo). A longer distance between neighbour Pd atoms leads to a weaker overlap of the d orbitals which causes an up-shift in *d*-band center position and this also explains the higher value of *d*-band center position for PdZn alloy besides the perspective of *d*-band filling factor as shown in Figure 6-10.

**Table 6-7** Typical lattice parameters of Pd<sub>3</sub>M alloys.

| M element in Pd <sub>3</sub> M | Bulk lattice parameter (Å) | Surface 2D parameter (Å) |
|--------------------------------|----------------------------|--------------------------|
| <b>Pd</b>                      | 3.952                      | 11.179                   |
| <b>Fe</b>                      | 3.891                      | 11.005                   |
| <b>Co</b>                      | 3.872                      | 10.952                   |
| <b>Ni</b>                      | 3.899                      | 11.028                   |
| <b>Zn</b>                      | 3.916                      | 11.076                   |

Due to the relatively high reduction potential of Ni(II) to Ni(0) ( $E^0[\text{Ni}(2+)/\text{Ni}(0)] = -0.25 \text{ V}$ ), the reduction behavior of Ni(II) is hard to control and the concentration of Ni(0) in the PdNi bimetallic cluster is much higher than other secondary atoms. The calculation model used for the PdCo alloys with various compositions is also applied to investigate the *d*-band structure of PdNi over a wide range of Ni content and the result is shown in Table 6-8.

**Table 6-8** Calculated *d*-band structure of a series of PdNi bimetallic NPs with variable composition.

| Sample                               | <i>d</i> -band filling | Surface <i>d</i> -band center (eV) |
|--------------------------------------|------------------------|------------------------------------|
| <b>Pd</b>                            | 0.88                   | -1.36                              |
| <b>Ni<sub>1</sub>Pd<sub>15</sub></b> | 0.88                   | -1.28                              |
| <b>Ni<sub>1</sub>Pd<sub>3</sub></b>  | 0.88                   | -1.24                              |
| <b>Ni<sub>1</sub>Pd<sub>1</sub></b>  | 0.88                   | -1.12                              |
| <b>Ni<sub>3</sub>Pd<sub>1</sub></b>  | 0.88                   | -1.06                              |

As shown above, the *d*-band filling of PdNi is kept at 0.88, due to the same number of valence electrons in Pd and Ni. But the *d*-band center position rises with the increasing concentration of Ni.

The catalytic results of the supported PdCo bimetallic nanoparticles containing various amount of Co were summarized in Table 6-9 and Figure 6-12a. The ethanol selectivity increases with respect to the increased number of neighbour Co around Pd in PdCo bimetallic NPs. The calculated values of “selective cleavage of C-O: selective cleavage of C-C” in term of ethanol selectivity: methanol selectivity ratios are displayed in Figure 6-12b and the value increases linearly with the number of neighbour Co around each absorbing Pd. This clearly suggests the enhanced ability of PdCo catalyst in breaking C-O bond over C-C bond of the substrate is correlated with increasing Co content.

**Table 6-9** Catalytic performance of a series of supported PdCo samples in the hydrogenolysis of EG (0.50 g catalyst; 30 mL of EG solution (5 wt%); 50 bar H<sub>2</sub> (r.t.); 250 °C for 24 h).

| Catalyst<br>(5 wt% Pd)                         | Conv.<br>% | Select. %<br>CH <sub>3</sub> OH | Select. %<br>C <sub>2</sub> H <sub>5</sub> OH | Select. %<br>CO <sub>2</sub> | Select. %<br>CH <sub>4</sub> | Select. cleave<br>of C-O:C-C | Select. %<br>total alcohols |
|------------------------------------------------|------------|---------------------------------|-----------------------------------------------|------------------------------|------------------------------|------------------------------|-----------------------------|
| <b>Sample 2,<br/>NCo=2.0<br/>(16.3 wt% Co)</b> | 31.2       | 35.9                            | 12.7                                          | 30.9                         | 18.7                         | 0.35                         | 48.6                        |
| <b>Sample 3<br/>NCo=3.1<br/>(24.6 wt% Co)</b>  | 34.2       | 19.0                            | 23.8                                          | 37.8                         | 18.5                         | 1.25                         | 41.8                        |
| <b>Sample 4<br/>NCo=4.9<br/>(36.0 wt% Co)</b>  | 25.3       | 14.3                            | 51.1                                          | 21.7                         | 12.3                         | 3.57                         | 65.4                        |
| <b>Sample 5<br/>NCo=4.7<br/>(51.3 wt% Co)</b>  | 20.7       | 13.1                            | 46.2                                          | 21.3                         | 18.4                         | 3.53                         | 59.3                        |

*(conv. and select. are abbreviations of conversion and selectivity, respectively)*

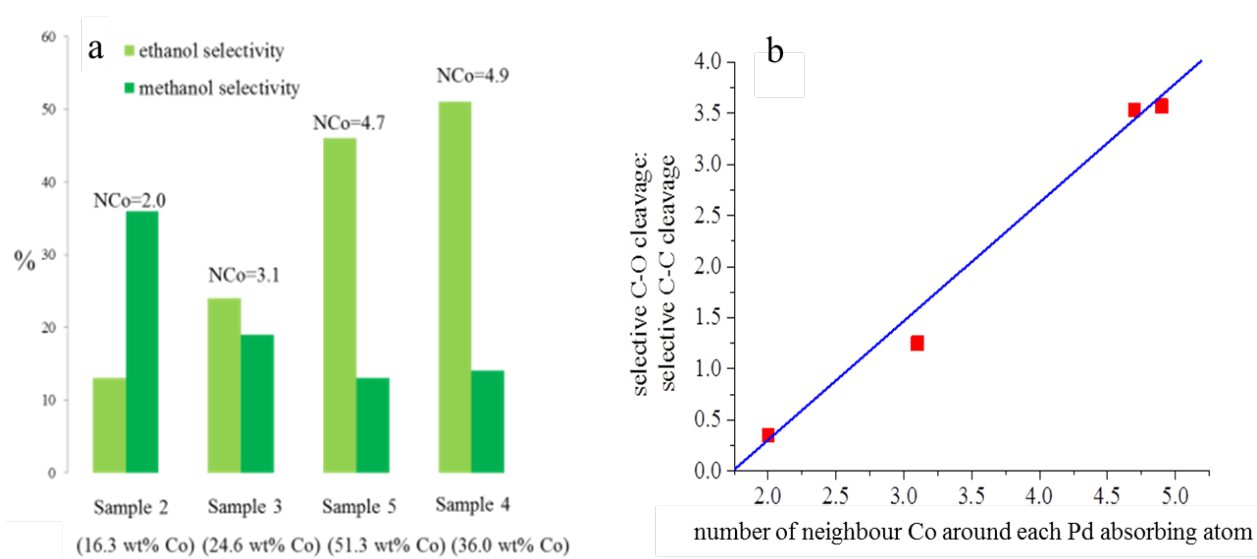


**Figure 6-12** (a) The variation of selectivity of methanol and ethanol in the hydrogenolysis of EG with Co content in PdCo catalyst. (b) Plot of “selective C-O cleavage: selective C-C cleavage” (ethanol selectivity/methanol selectivity) against the number of neighbour Co around Pd from the EXAFS data.

Through the optimization of the reaction conditions for sample 4 (36.0 wt%), it is observed that the ethanol selectivity rises with the downshift of reaction temperature. Also, it increases with the increasing amount of used catalyst corresponding to an increasing ratio of noble metal catalyst to the substrate (EG). A 70% ethanol selectivity with a high value of “selective cleavage of C-O: selective cleavage of C-C” over 8 is achieved on sample 4 (36.0 wt%) and the total alcohol selectivity reaches around 80% (as shown in Table 6-10) after the optimization of reaction condition. The catalytic performance makes PdCo bimetallic NPs (with high content of Co) a promising catalyst for selective C-O bond breaking in biomass hydrogenolysis.

**Table 6-10a** Catalytic performance of sample 4 (36.0 wt% Co) in the hydrogenolysis of EG with variable temperature (0.50 g catalyst; 30 mL of EG solution (5 wt%); 50 bar H<sub>2</sub> (r.t.) for 24 h).

| Temperature (°C) | Conv. % | Select. % CH <sub>3</sub> OH | Select. % C <sub>2</sub> H <sub>5</sub> OH | Select. % CO <sub>2</sub> | Select. % CH <sub>4</sub> | Select. cleave of C-O:C-C | Select. % total alcohols |
|------------------|---------|------------------------------|--------------------------------------------|---------------------------|---------------------------|---------------------------|--------------------------|
| 250              | 25.3    | 14.3                         | 51.1                                       | 21.7                      | 12.3                      | 3.57                      | 65.4                     |
| 245              | 11.0    | 13.0                         | 51.0                                       | 16.3                      | 19.4                      | 3.92                      | 64.0                     |
| 240              | 6.2     | 11.4                         | 60.3                                       | 14.7                      | 12.5                      | 5.29                      | 71.7                     |
| 235              | 5.8     | 8.0                          | 67.0                                       | 9.7                       | 14.7                      | 8.37                      | 75.0                     |

**Table 6-10b.** Catalytic performance of sample 4 (36.0 wt% Co) in the hydrogenolysis of EG with various mole ratio of Pd catalyst: substrate (30 mL of EG solution (5 wt%); various amount of catalyst; 50 bar H<sub>2</sub> (r.t.); 240°C for 24 h).

| Mole ratio of Pd: EG | Conv. % | Select. % CH <sub>3</sub> OH | Select. % C <sub>2</sub> H <sub>5</sub> OH | Select. % CO <sub>2</sub> | Select. % CH <sub>4</sub> | Select. cleave of C-O:C-C | Select. % total alcohols |
|----------------------|---------|------------------------------|--------------------------------------------|---------------------------|---------------------------|---------------------------|--------------------------|
| 0.005                | 4.7     | 14.6                         | 44.0                                       | 23.2                      | 16.6                      | 3.01                      | 65.4                     |
| 0.010                | 6.2     | 11.4                         | 60.3                                       | 14.7                      | 12.5                      | 5.29                      | 71.7                     |
| 0.015                | 13.4    | 6.0                          | 67.0                                       | 20.9                      | 5.1                       | 11.17                     | 73.0                     |
| 0.020                | 35.2    | 8.6                          | 70.0                                       | 18.2                      | 3.4                       | 8.14                      | 78.6                     |

*(conv. and select. are abbreviations of conversion and selectivity, respectively)*

We have calculated the effect of progressive substitution of the top surface Pd atoms with Co atoms on the surface *d*-band structure of Pd-based bimetallic NPs on a 4×4×4 atomistic model by

density functional theory (DFT) (Scheme 6-2). The compiled surface *d*-band center position and *d*-band filling of Pd in a series of PdCo bimetallic nanoparticles are displayed in Figure 6-13. The surface *d*-band center upshifts significantly at high degree of Co substitution. This is consistent with the prediction from the *d*-band center theory that the center gravity of PdCo will shift to higher energy level because of the dominant effect of mixing higher energy orbital of Co 3d with that of Pd 4d (ligand effect). [47] But the total degree of electron filling for the new hybrid *d*-band of PdCo only shows a minor decrease, presumably due to the similar number of valence electrons for Pd (10 valence electrons) and Co (9 valence electrons). Consequently, it is evident from our study that the progressive uplift of the *d*-band center at high Co content can increase the C-O cleavage: C-C cleavage ratio in the catalytic hydrogenolysis of EG accordingly. Note that the recent density functional theory (DFT) calculations in literature suggest that the adsorption kinetics of C-O bonds of EG is much more favoured than both C-H and C-C adsorptions over the extended (111) metal surfaces. This facilitates the activation of C-O bonds but destabilizes the approach of  $\alpha$ C in C-C of the molecule at the terrace metal sites.[48] However, in this thesis, it is argued that the contribution of this geometric reasoning may not be significant in our case as the relaxation of the steric constraints on the ‘nano-size’ bimetallic particles should also facilitate C-C activation. This leads to the scission of C-C bond followed by the C-H formation which produces methanol. Nevertheless, from our results, the upshift of *d*-band center position is undoubtedly the key parameter in determining the extent of C-C and C-O cleavage.

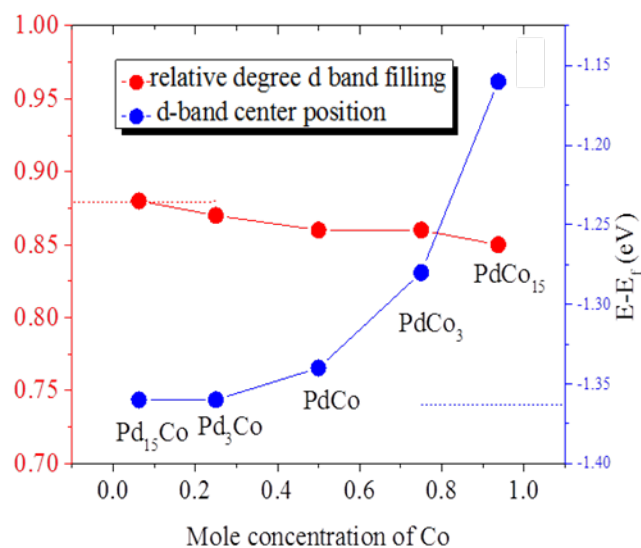


**Figure 6-13** Calculated *d*-band filling and *d*-band center position of PdCo with different Co content (the corresponding values of Pd are labelled in the figure as dash lines).

The corresponding calculated surface density of states (DOS) diagrams for the PdCo bimetallic NPs are shown in Figure 6-14. The density of states clearly shifts to a higher position with increasing concentration of Co due to the higher energy level of Co 3d than that of Pd 4d.

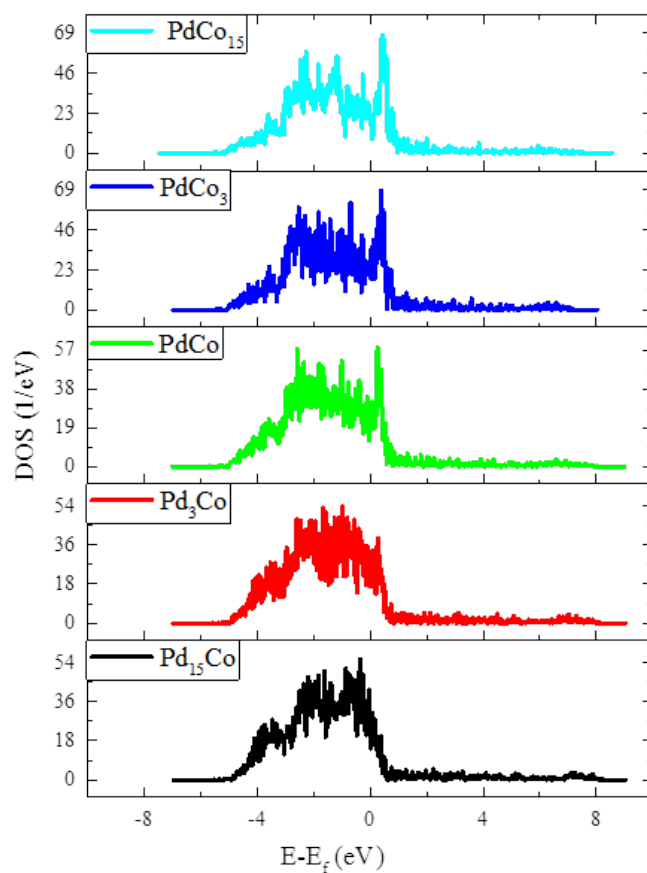


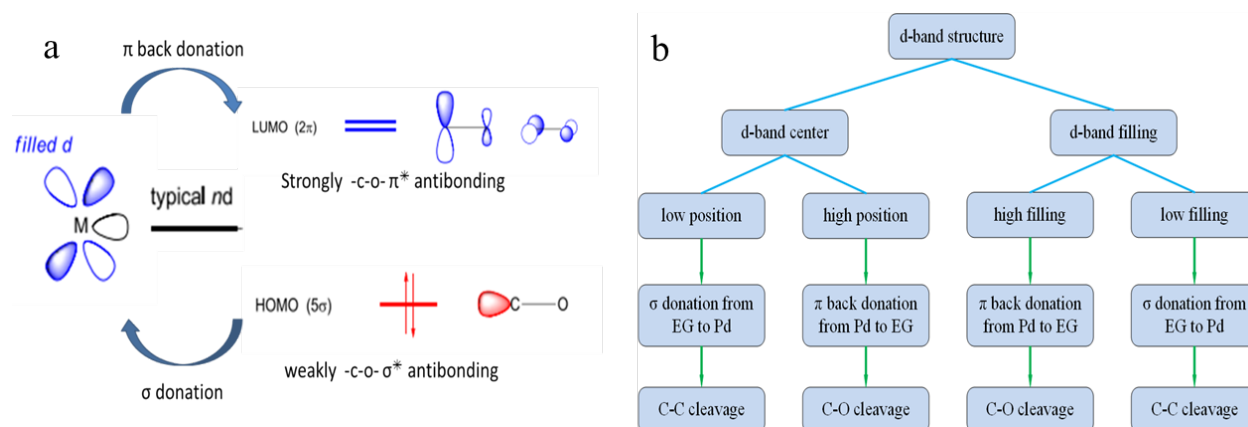
**Figure 6-14** Calculated surface density of states (DOS) diagrams of a series of PdCo alloys with variable composition.

From the catalytic results and the theoretical electronic structure calculations, it is concluded the catalytic ability of Pd in selective C-O cleavage over C-C cleavage increases with the upshift of both *d*-band center position and the *d*-band filling. In contrast, the selective C-C breakage in hydrogenolysis of the vicinal diol unit is mainly achieved through the significant reduction of *d*-band filling of Pd by alloying with early transition metals. Presently, the quantitative assessments of the *d*-band filling and the *d*-band center position in relation to a particular type of bond cleavage have not yet been achieved due to the

interplay of these two important factors as well as the challenge for fine control in synthesis. However, it is believed that this analysis could guide the refinement of the synthesis for catalytic materials needed for selective C-C or C-O bond cleavage in biomass activation.

## 6.5 Discussion

Apparently, the propensity of the PdM alloy catalysts for hydrogenolytic C-O or C-C bond cleavage in EG is directly governed by their electronic interaction with the substrate molecule (in particular, the C-O function group) as demonstrated in Scheme 6-3(a). Through the hybridization of *d* orbitals, the neighbour secondary atoms M (M = Fe, Co, Zn) are expected to modify the *d*-band structure of PdM bimetallic phase from monometallic Pd significantly. The *d*-band filling increases from PdFe to PdCo, PdNi and PdZn due to increasing number of valence electrons in the transition metals ( $\text{Fe } 3d^6 4s^2 < \text{Co } 3d^7 4s^2 < \text{Ni } 3d^8 4s^2 < \text{Zn } 3d^{10} 4s^2$ ). It is anticipated that the increasing *d*-band filling enables electronic  $\pi$  back donation to the strong anti-bonding  $\pi^*$  orbital of the adsorbed -C-O- moiety, which facilitates the C-O bond activation. Meanwhile, the electron donation from the adsorbate through Pd-C bond to the metal would be disfavoured due to the increased *d*-band filling, which would also reduce the tendency for the C-C bond cleavage. This could account for the observation that the value of “selective cleavage of C-O: selective cleavage of C-C” increases with the *d*-band filling of PdM as  $\text{PdFe} < \text{PdCo} < \text{PdNi} < \text{PdZn}$ . Besides *d*-band filling, the *d*-band center position is also found significantly affecting the bond cleavage tendency. The upshifted *d*-band center position of Pd is expected to match better with the  $\pi^*$  orbital of C-O which eventually enhances the  $\pi$  back donation from Pd to the empty  $\pi^*$  orbital. This strengthens the breakage of the C-O bond in EG. Therefore, the value of “selective cleavage of C-O: selective cleavage of C-C” increases with the up-shift of *d*-band center by increasing Co content in PdCo bimetallic NPs reaches maximum at sample 4 (36.1 wt% Co).



**Scheme 6-3** (a) Electronic interaction of Pd and the  $-C-O-$  function group of EG; (b) the relationship between the  $d$ -band structure of Pd and the catalytic properties.

## 6.6 Conclusions

The ability of Pd in selectively breaking C-O bond over C-C bond of EG in hydrogen can be tailored with a good degree of accuracy. By rationally tuning the SMSI between Pd NPs and the supports, a wide range of PdM bimetallic NPs with tunable compositions can be prepared. The progressive upshift of  $d$ -band center position as well as the increased  $d$ -band filling of Pd metal through the incorporation of a late 1<sup>st</sup> row transition metal element would gradually favour C-O cleavage. On the other hand, the decrease in  $d$ -band filling of Pd by interacting with an early transition metal would favour C-C cleavage. The relationship between the  $d$ -band structure of Pd and the catalytic properties are summarized in Scheme 6-3b. The tunability of the Pd-based catalysts by SMSI for hydrogenolysis of ethylene glycol is clearly demonstrated.

As stated, there is an increasing interest in both academic and industrial communities to transform biomass molecules to fuel and commodity chemicals, particularly using the heterogeneous catalytic hydrogenolysis reaction route. However, there is very limited literature to guide the selection of catalysts for any target product. There have been considerable

experimental efforts in synthesizing a wide variety of catalysts, but it is very difficult, if not impossible, to exhaust all of the possibilities by a trial-and-error approach. This study has employed ethylene glycol as a substrate model, which represents for the basic repeating units in macroscopic biomass molecule. By rationally tuning the SMSI (which promotes the formation of PdM bimetallic NPs), it illustrates, for the first time, the possibility of fine-tuning of electronic factors in product specificity for catalytic biomass utilization.

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# **Chapter 7 A Non-syngas Biomass-based Process of Methanol Production over Pd@Zn Nano-composite**

## **Overview**

Methanol is a key commodity in industry due to its position as synthetic intermediate for a wide variety of chemicals and also as a clean transportation fuel owing to its high energy density. At present, methanol is manufactured from natural gas via the syn-gas route under high pressure (5-10 MPa) and high temperature, which uses non-renewable resource and is energy inefficient. In this chapter, we will show the production of methanol from biomass utilization via CO<sub>2</sub> hydrogenation route over a novel Pd@Zn core-shell bimetallic catalyst. The CO<sub>2</sub>/H<sub>2</sub> gas with generated pressure of 20 bar is obtained by the low temperature reforming of biomass molecules. For the Pd@Zn catalyst, the Zn shell is derived from the reduction of ZnO support for Pd clusters. Through the establishment of a CdSe-ZnO hetero-junction, the thickness of Zn shell can be well-tuned by varying the ratio of ZnO: CdSe in the support. The decoration of Pd clusters by Zn shell not only promotes the rate of methanol formation on the bimetallic phase from CO<sub>2</sub> hydrogenation, but also significantly suppresses the CO production rate (from RWGS). This eventually results in a methanol turnover frequency (TOF) of  $3.3 \times 10^{-1} \text{ s}^{-1}$  with high selectivity over 75% at 4.5 MPa on Pd sites. At a lower pressure of 2.0 MPa, methanol can still be produced as the main product over CO with a decent activity (TOF =  $1.9 \times 10^{-1}$ ). This excellent catalytic property is ascribed to the high electron density which stabilizes -HCOO- (the intermediate to

methanol) selectively rather than -COOH- (the precursor of CO) on the PdZn surface with a high activity of H<sub>2</sub> activation.

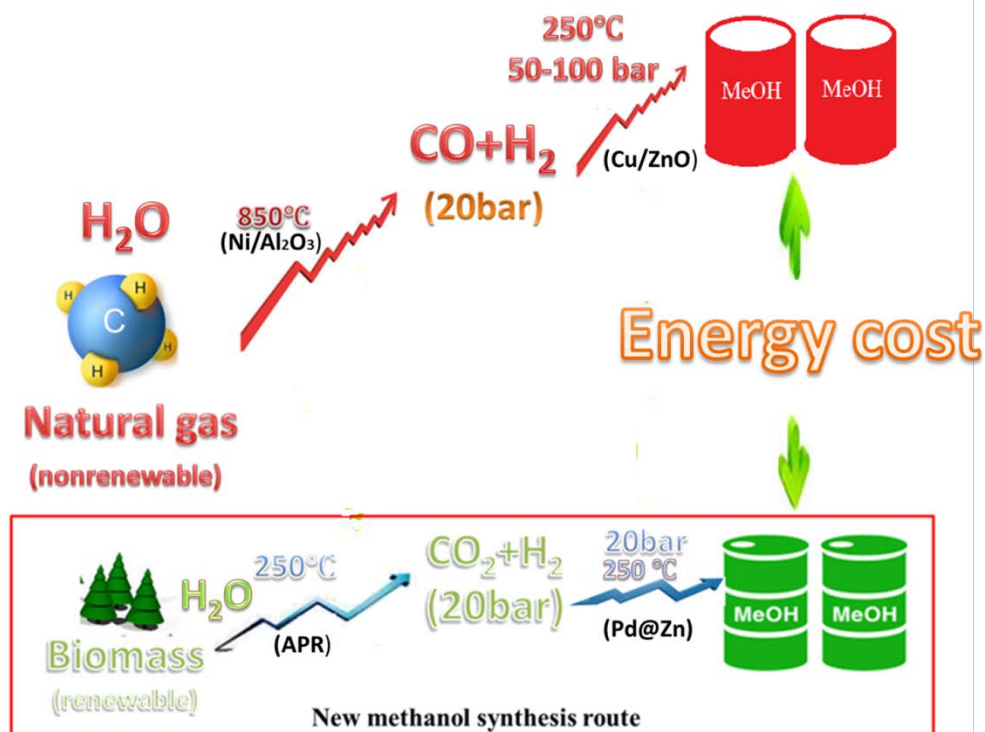
The catalytic performance of this Pd@Zn nano-composite is superior to that of the conventional Cu/ZnO catalyst. It opens up a possibility in renewable methanol synthesis from biomass utilization under mild conditions.

## 7.1 Introduction

Catalytic methanol production is one of the most important reactions in industry due to the wide application of methanol in fuel and chemical synthesis. [1, 2] Currently, methanol is produced by two steps. First, a high temperature process is required to break down the resilient methane molecule (natural gas) to synthesis gas (CO/H<sub>2</sub> syn-gas) by steam reforming over Ni based catalyst at >850°C at 2 MPa. Second, the syngas is rearranged to methanol over Cu/ZnO catalyst at 250°C at 5-10 MPa.[3,4,5] Thus, the process uses non-renewable resource, and is highly energy inefficient.[1,6,7,8] Also, the conditions for the two reaction steps are non-compatible to each other since the latter step of transforming synthesis gas into methanol requires a higher pressure. Therefore, the cost for pumping and cumbersome equipment significantly reduces the profit margins. ***It would be highly attractive to develop a renewable synthetic route for methanol production under relatively mild condition (low working temperature and pressure).*** As one of the primary renewable energy resources, biomass is generally regarded as a promising alternative to the fossil fuels.[9] Recently, the low temperature activation of biomass has been achieved in industry producing CO<sub>2</sub>/ H<sub>2</sub> (CO<sub>2</sub>:H<sub>2</sub> = 1:2) as the products with a generated pressure of 20 bar. Thus, the key step of methanol synthesis from biomass lies in catalytic CO<sub>2</sub> hydrogenation:  $\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$ . Due to the position

of CO<sub>2</sub> as the primary greenhouse gas causing climate change, this reaction has attracted increased attention with the developments of renewable H<sub>2</sub> production and low cost CO<sub>2</sub> capture. [10, 11] Some significant progresses have been achieved. As carefully reviewed by Masahiro Saito *et al.*, Cu/ZnO based catalysts are not only demonstrated to be active for CO/H<sub>2</sub> conversion but they also exhibit superior activity in CO<sub>2</sub> hydrogenation to methanol among a wide variety of catalysts.[12] Recently, Cu steps decorated with Zn atoms have been identified as the active sites. The methanol TOF on the Cu site with decoration of Zn reaches  $2.0 \times 10^{-2} \text{ s}^{-1}$  at 6 MPa whereas a low value of  $5.4 \times 10^{-4} \text{ s}^{-1}$  for pure Cu.[13] A new model Cu/CeO<sub>x</sub> catalyst is reported to show an even higher TOF value. [14] The excellent catalytic performance of this Cu/CeO<sub>x</sub> catalyst, however, requires a very high ratio of H<sub>2</sub>:CO<sub>2</sub> (around 9), which is not practical in methanol synthesis from biomass generated CO<sub>2</sub>/H<sub>2</sub> mixtures (with a H<sub>2</sub>:CO<sub>2</sub> ratio of 2-3). In addition to the activity of catalyst, what is more problematic is the low methanol selectivity owing to the simultaneous rapid production of CO through the reverse water gas shift reaction (RWGS) route ( $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$ ), particularly under relatively low pressure. For the Cu-based catalysts, 70% methanol selectivity usually requires a pressure over 7 MPa. [12] Unfortunately, the biomass generated CO<sub>2</sub>/H<sub>2</sub> is usually under 2 MPa. (the reforming of biomass molecule is a reaction with volume expansion, thus requires low pressure to maintain the biomass conversion). The extra compression of CO<sub>2</sub>/H<sub>2</sub> gas is expensive and time consuming. With a reaction pressure lower than 2 MPa, the rate of RWGS is observed to be 1-3 orders of magnitude higher than that of methanol synthesis on CuZn surface. [15] This leads to an extremely low methanol selectivity (usually under 10% at 2 MPa) and results in a waste of CO<sub>2</sub>/H<sub>2</sub> stock, and consequently increases cost despite the decent activity towards methanol formation. Therefore, the low specificity of the catalyst for methanol synthesis and the cost for

high pressure are the main challenges in CO<sub>2</sub> hydrogenation which block the green methanol synthesis from biomass utilization. In this chapter, we present a series of supported Pd@Zn core-shell bimetallic particles with various compositions which are active catalysts in CO<sub>2</sub> hydrogenation. The Zn decoration on Pd surface offers a higher kinetic barrier for RWGS reaction to reduce CO levels but facilitates CH<sub>3</sub>OH formation. Methanol selectivity over 75% has been achieved at 4.5 MPa with a methanol TOF of  $3.3 \times 10^{-1} \text{ s}^{-1}$  on the Zn decorated Pd site. This TOF value is 80 fold higher than that of Cu in the industrial Cu/ZnO catalyst, and is also the highest value found in literature (at a H<sub>2</sub>:CO<sub>2</sub> ratio  $\sim 2.8$ ). Due to the suppression of CO production by Zn decoration, methanol selectivity on Pd@Zn catalyst can be maintained at ca. 70% as compared to 10% over Cu catalyst when the pressure decreases to 2.0 MPa. Meanwhile, the methanol TOF of Pd ( $1.9 \times 10^{-1} \text{ s}^{-1}$ ) is observed to be 350 times higher than that of Cu in the commercial Cu/ZnO catalyst at 2.0 MPa. Using this novel Pd@Zn catalyst, the biomass generated CO<sub>2</sub>/H<sub>2</sub> can be converted into methanol directly without further compression. Therefore, a convenient renewable methanol synthesis route with high energy efficiency (low temperature) and low cost (low pressure) can be established. The comparison of the proposed biomass route with the traditional syngas route for methanol synthesis is shown in Scheme 7-1. Undoubtedly, the proposed route shows advantages over the traditional one from the viewpoint of energy cost.



**Scheme 7-1** The proposed new methanol synthesis route from biomass and the comparison with the traditional syn-gas route. (APR is abbreviation of aqueous phase reforming reaction.)

## 7.2 Synthesis of materials

The supported Pd@Zn bimetallic particles are synthesized through the reduction of PdO/rodlike ZnO precursor which is obtained by an impregnation method as described in Chapter 3. The reduction of PdO to Pd(0) can be completed readily at room temperature, after which the produced Pd particles catalyze the reduction of ZnO to Zn(0) at the elevated temperature. A type II hetero-junction of ZnO-CdSe is established in the support to control the amount of produced Zn(0) atoms. The thickness of Zn shell on Pd surface is governed by the ratio of ZnO: CdSe in the support.

## 7.3 Characterization of ZnO-CdSe supports

### 7.3.1 Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

ICP-AES was used to determine the ratio of ZnO: CdSe in a series of samples as shown in Table 7-1.

**Table 7-1** ICP-AES results of a series of ZnO-CdSe supports.

| Sample | CdSe wt% | ZnO: CdSe |
|--------|----------|-----------|
| 1      | 0.0      | N.A.      |
| 2      | 9.4      | 22.4      |
| 3      | 19.2     | 10.0      |
| 4      | 26.4     | 6.6       |

*(N.A.: Not applicable.)*

### 7.3.2 Transmission Electron Microscopy (TEM)

The HR-TEM images of sample 1 (0.0 wt% CdSe) and sample 4 (26.4 wt% CdSe) without Pd loading are displayed in Figure 7-1. Without the addition of CdSe quantum dot, rod ZnO (sample 1(0.0 wt% CdSe)) are clearly found and the lattice fringe of 0.32 nm (Figure 7-1b) was assigned to the lattice distance of ZnO on the a- and b-axes of wurtzite structure.[16] From the images of sample 4 (26.4 wt% CdSe) (Figure 7-1c,d), the preformed 4±1 nm CdSe nanoparticles with lattice fringe of 0.30 nm (CdSe (101)) are embedded and dispersed in rod ZnO.[17] This suggests that our sequential synthesis method was successful in burying CdSe into ZnO rod crystals.

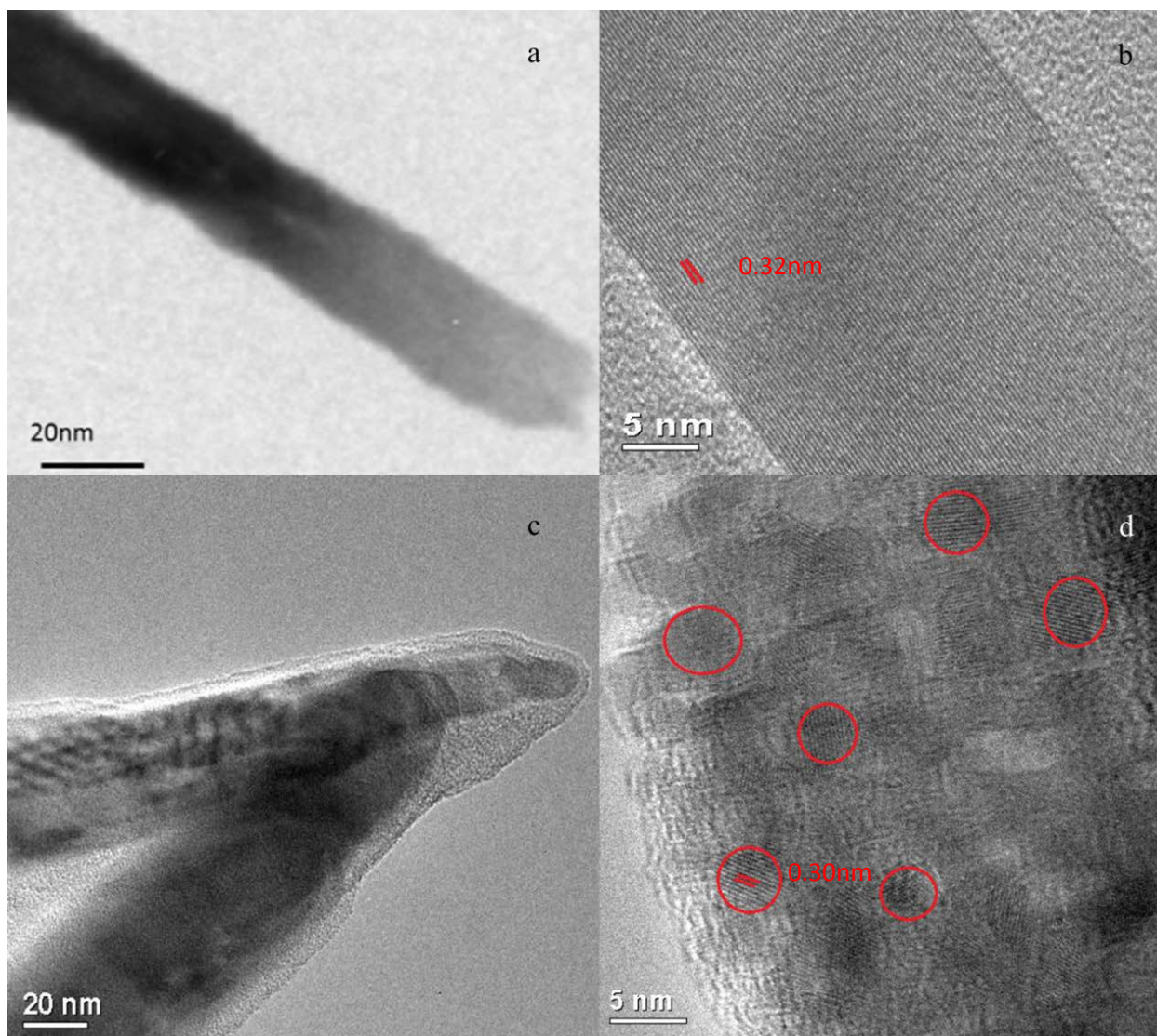


**Figure 7-1** TEM and HRTEM of (a, b) sample 1 (0.0 wt% CdSe) and (c, d) sample 4 (26.4 wt% CdSe) before the Pd loading.

### 7.3.3 Diffuse Reflectance Spectroscopy (DRS)

As shown in Figure 7-2a, sample 1 (0.0 wt% CdSe) gives a typical ZnO absorption edge at 380nm. For samples 2-4 with the addition of CdSe, another one around 650 nm in the visible region was observed which reflects the existence of CdSe in the supports with a band gap of 1.7-

1.9 eV. The relative energy positions of the conduction and valence bands of CdSe and ZnO are shown in Figure 7-2b. A typical type II hetero-junction is formed due to the staggered energy levels in proximity.

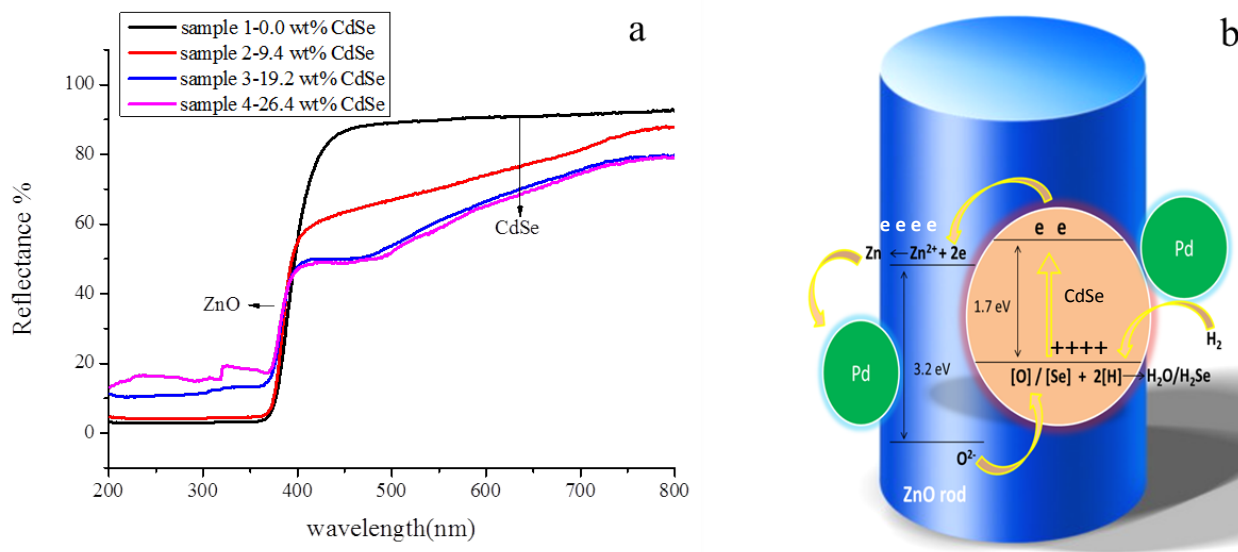


**Figure 7-2** (a) DRS profiles for a series of ZnO-CdSe support; (b) the energy levels alignment of CdSe core and ZnO shell.

### 7.3.4 Time-Resolved Photoluminescence (TRPL)

As stated in Chapter 4, the type II hetero-junction favours a specific charge separation.[18-20] As illustrated in Figure 7-2b, the excited electrons (e) reside in the conduction band of ZnO, whilst the holes(+) in the valence band of CdSe. Therefore, the recombination rate of electrons and holes is expected to decrease due to the excitons separation across the interface. Thus, the lifetime of excitons in ZnO-CdSe material is supposed to be extended with reference to the single phase of ZnO. [21] TRPL was employed to verify the hetero-junction effect. The TRPL spectra and the corresponding kinetic decay profiles at 425-850 nm for sample 4 (26.4 wt% CdSe) with the largest amount of CdSe-ZnO hetero-junction interfaces and sample 1(0.0 wt% CdSe) (used as

the reference without hetero-junction) are shown in Figure 7-3. The derived lifetime parameters by curve fitting are summarized in Table 7-2. [22, 23] It is clear that the lifetimes of excitons in material are extended by the addition of CdSe. Sample 4 (26.4 wt% CdSe) shows longer time constants than sample 1(0.0 wt% CdSe), which confirms the hetero-junction effect in ZnO-CdSe structure.

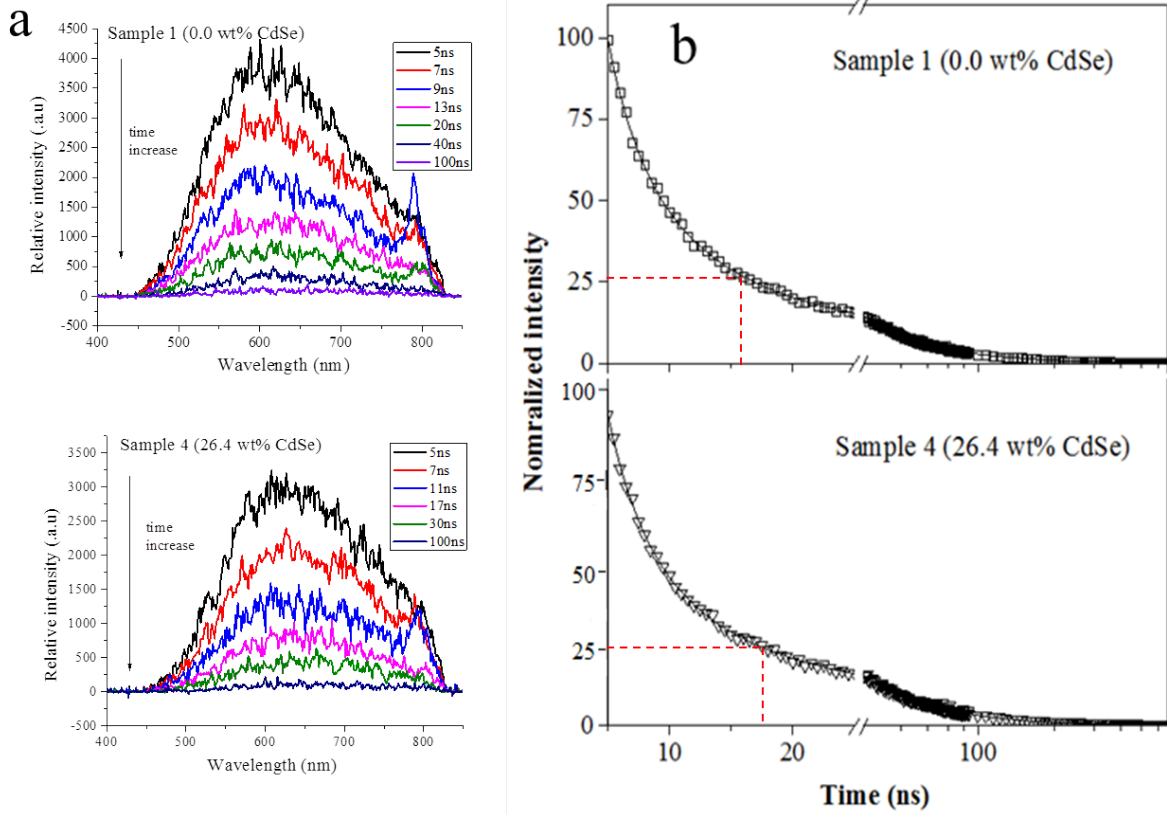


**Figure 7-3** (a) Time-resolved emission spectra of sample 1(0.0 wt% CdSe) and sample 4 (26.4 wt% CdSe) in the solid state at delay times within hundreds nanoseconds after excitation at 300 nm; (b) Experimental and fitted (solid lines) kinetic decay profiles of sample 1(0.0 wt% CdSe) and sample 4 (26.4 wt% CdSe).

**Table 7-2** Decay time constants ( $\tau$ ) and the amplitude parameters (a%) obtained from the decay profile of sample 1 (0.0 wt% CdSe) and sample 4 (26.4 wt% CdSe).

| Sample                             | $\tau 1(\text{ns})$<br>(a1%) | $\tau 2(\text{ns})$<br>(a2%) | $\tau 3(\text{ns})$<br>(a3%) | $\tau 4(\text{ns})$<br>(a4%) |
|------------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|
| <b>1</b><br><b>(0.0 wt% CdSe)</b>  | 2<br>(65%)                   | 6<br>(27%)                   | 22<br>(7%)                   | 115<br>(1%)                  |
| <b>4</b><br><b>(26.4 wt% CdSe)</b> | 3<br>(70%)                   | 9<br>(23%)                   | 34<br>(6%)                   | 152<br>(1%)                  |

With the extended excitons lifetime of ZnO-CdSe hetero-junction, more electrons and holes are accumulated on the surface of ZnO and CdSe, respectively, due to the slowed recombination rate across the interface. By the spilled atomic H from the neighbour Pd, the holes in CdSe rich area existing as Se or O species with lower formal charge could be eliminated to form  $\text{H}_2\text{Se}$  or  $\text{H}_2\text{O}$  as the lifetime constant is long enough to allow the occurrence of these chemical reactions. Correspondingly, electrons in ZnO rich area will reduce Zn ions to Zn metal atoms. The proposed reduction mechanism of the hetero-junction support is shown in Figure 7-2b. The detailed information of controllable reduction of metal oxide facilitated by hetero-junction support is thoroughly described in Chapter 4.

## 7.4 Characterization of Pd@Zn structures

### 7.4.1 X-ray Photoelectron Spectroscopy

5 wt% Pd was loaded on a ZnO-CdSe support by impregnation method. The Pd@Zn bimetallic phase was produced after the pre-reduction. XPS was employed to detect the oxidation state of Zn after pre-reduction as shown in Figure 7-4 (left). Among the reduced Pd/ZnO-CdSe samples (5 wt% Pd) with various ratios of ZnO: CdSe, the binding energy of Zn shifts to a lower value

progressively with respect to the increasing CdSe content (with reference to the added boron nitride (BN), N 398.2 eV). After curve fitting analysis (Figure 7-4 (right)), each Zn spectrum was fitted into 2 peaks; one at 1021.3 eV corresponds to the Zn (II) signal and the other one at 1020.1 eV to metallic Zn(0). [24] The ratios of the two peaks (Zn (0): Zn(II)) are shown in Table 7-3. The value increases from 0.14 of sample 1 (5 wt% Pd, 0.0 wt% CdSe) to 2.8 of sample 4 (5 wt% Pd, 26.4 wt% CdSe) reflecting the promotion of Zn(II) reduction to Zn (0) by CdSe.

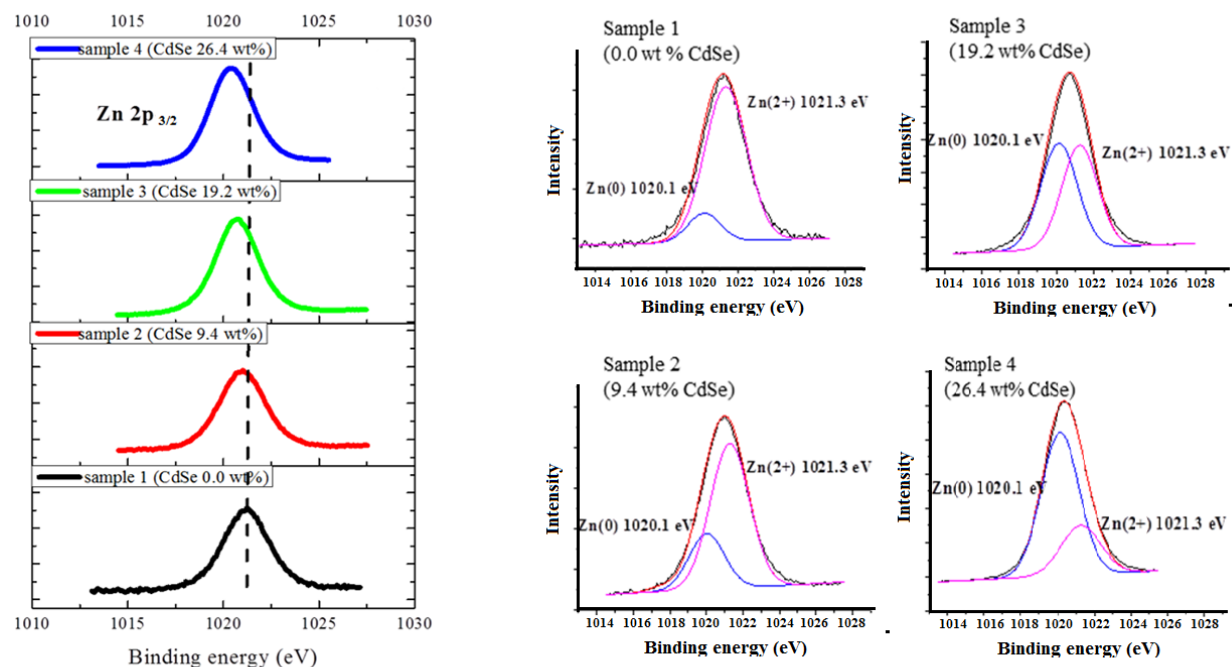


**Figure 7-4** (Top, left) XPS curves of Zn in a series of reduced Pd/ZnO-CdSe (5 wt% Pd) samples. (Top, right) the corresponding fitting curves of Zn. (Bottom) The FWHM values for the whole Zn XPS curves, the fitted Zn(0) peaks and the fitted ZnO peaks, respectively.

**Table 7-3** Calculated ratios of Zn(0):Zn(II) from XPS results for a series of Pd/ZnO-CdSe samples.

| Sample No.   | 1<br>(0.0 wt% CdSe) | 2<br>(9.4 wt% CdSe) | 3<br>(19.2 wt% CdSe) | 4<br>(26.4 wt% CdSe) |
|--------------|---------------------|---------------------|----------------------|----------------------|
| Zn(0):Zn(II) | 0.14                | 0.35                | 1.0                  | 2.8                  |

#### 7.4.2 Transmission Electron Microscopy (TEM)

TEM images of reduced sample 1 (5 wt% Pd, 0.0 wt% CdSe) and sample 4 (5 wt% Pd, 26.4 wt% CdSe) are shown in Figure 7-5. Rod-like ZnO supports are observed and Pd containing particles with an average size of 3-4 nm are found to be anchored on the surface of ZnO rods for the two samples. In sample 4 (5 wt% Pd, 26.4 wt% CdSe), the Pd containing phase is composed of an imperfect core (dark)-shell (light) structure (Figure 7-5 bottom (d, e, f)). Clear lattice fringes of 0.23 nm and 0.26 nm can be observed on the core and the shell, respectively. The former value corresponds to the (111) plane of Pd while the latter matches the lattice distance of Zn metal (002) facet. [25, 26] This confirms the existence of metallic Zn in the reduced sample. The core-shell structure was constructed by the sequential growth of Zn(0) on the surface of previously formed Pd clusters due to the more negative redox potential of Zn(2+)/Zn(0) ( $E^0 = -0.76$  V) than that of Pd(2+)/Pd (0) ( $E^0 = +0.92$  V). At the core (Pd)-shell (Zn) interface (Figure 7-5 bottom (f)), a mixed phase with an irregular atom arrangement is formed implying the formation of a PdZn bimetallic phase. In contrast, almost no Pd@Zn core-shell structure is observed in TEM images (Figure 7-5 top) for reduced sample 1 (5 wt% Pd, 0.0 wt% CdSe). This is attributed to the much lower Zn content in this sample. The result is consistent with the result of XPS.

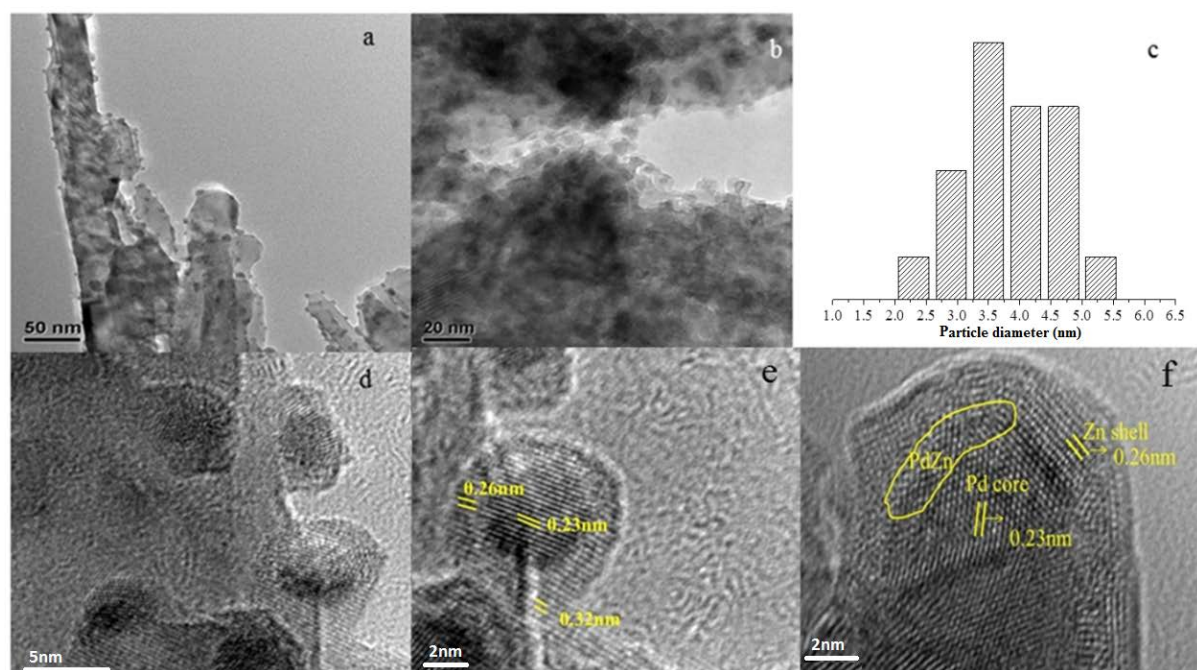
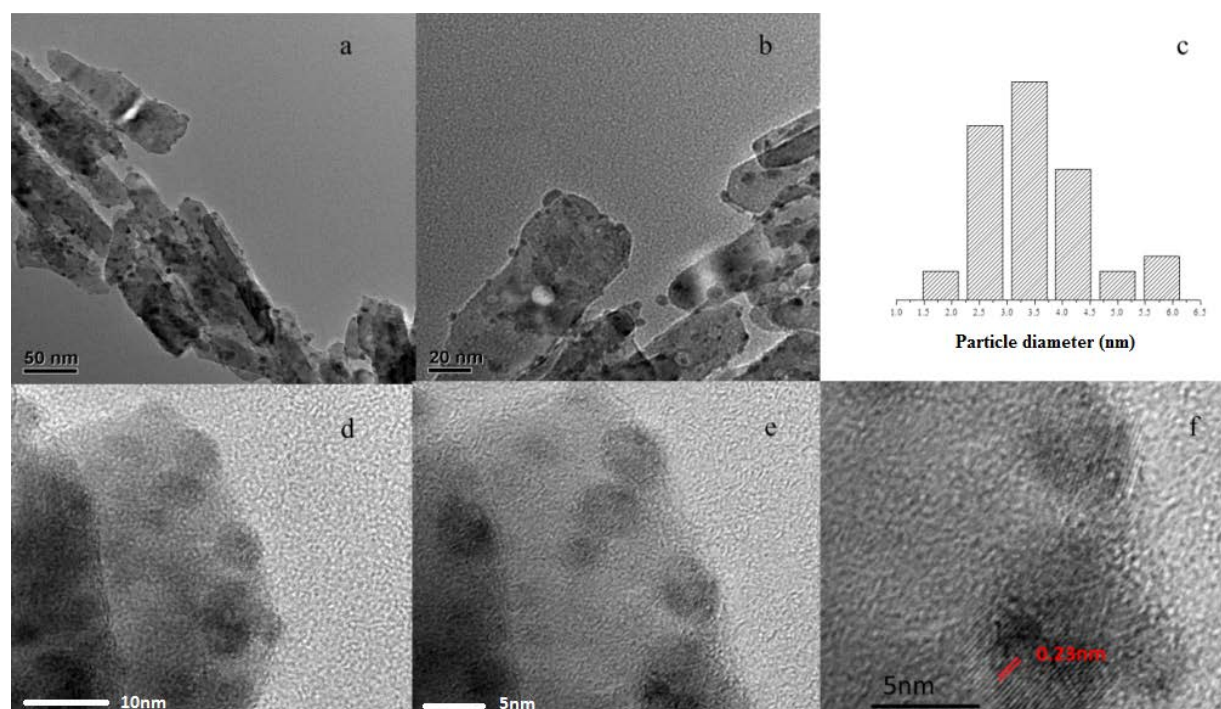


**Figure 7-5** (a,b) TEM and (d, e, f) HRTEM images for reduced (top) sample 1 (5 wt% Pd, 0.0 wt% CdSe) and (bottom) sample 4 (5 wt% Pd, 26.4 wt% CdSe); (c) the particle size distribution

of Pd particles in the two samples. (Note that the 0.32 nm lattice spacing in Figure 7-5 bottom e reflects the plane distance of ZnO.)

#### **7.4.3 Extended X-ray Absorption Fine Structure (EXAFS)**

The EXAFS at Pd K-edge (24350 eV) was employed to further investigate the coordination environment of Pd in a series of PdZn bimetallic NPs (Figure 7-6 and Table 7-4). All the samples show similar total coordination number (CN) of Pd in a range of 7-9. This corresponds to an estimated average size of 3 nm within acceptable R- and Debye Waller (D-W) factors. [27] The results are agreeable with TEM images. We also observed a shorter scattering path with 2.57 Å distance (Figure 7-6a) comparing with a typical 2.70 Å Pd-Pd scattering path in nano-sized Pd particles.[28] This shorter one is assigned to the first shell scattering pair of Pd-Zn. As shown in Figure 7-6b, the number of neighbour Zn (NZn) around each Pd absorbing atom increases with the concentration of added CdSe reaching the highest value in sample 4 (5 wt% Pd, 26.4 wt% CdSe). The result indicates the growing content of Zn in the bimetallic phase with CdSe addition which is consistent with the results of XPS and TEM.

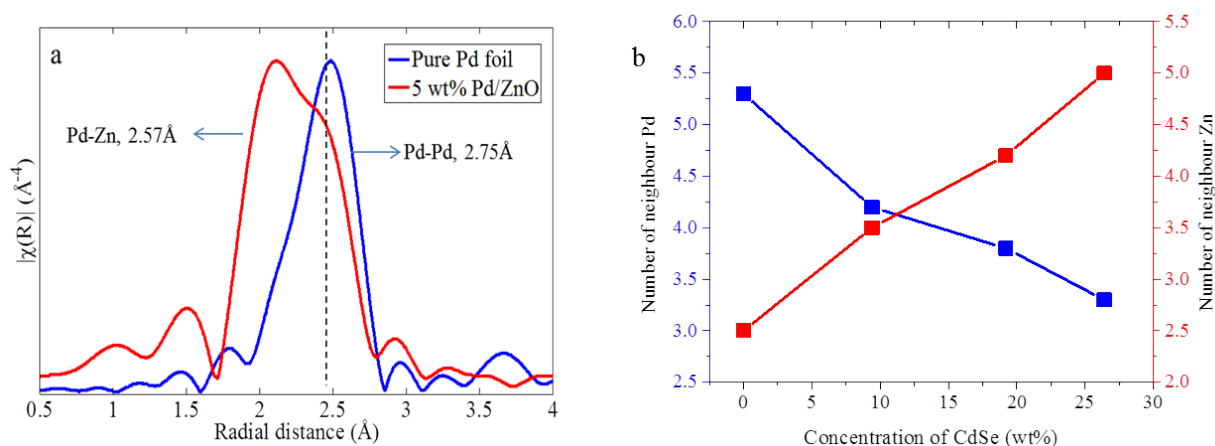


**Figure 7-6** (a) Fourier transform of the EXAFS curves (typical EXAFS curves against radial distance) for sample 1 (5 wt% Pd, 0.0 wt% CdSe) and a Pd foil ; (b) the number of neighbour Pd (NPd) and Zn (NZn) around each Pd absorbing atom derived from the EXAFS.

**Table 7-4** Average coordination environment of a Pd absorbing atom from the EXAFS results for a series of Pd/ZnO-CdSe samples

| Sample | Total CN | $\Delta E$<br>(eV) | Pd-Pd<br>distance (Å) | D-W<br>factor<br>(Å <sup>2</sup> ) | Pd-Zn<br>distance (Å) | D-W<br>factor(Å <sup>2</sup> ) | R-<br>factor |
|--------|----------|--------------------|-----------------------|------------------------------------|-----------------------|--------------------------------|--------------|
| 1      | 7.8(8)   | -5.0               | 2.67(1)               | 0.015(2)                           | 2.56(1)               | 0.004(1)                       | 2.1%         |
| 2      | 7.7(7)   | -4.5               | 2.71(1)               | 0.014(2)                           | 2.56(1)               | 0.008(1)                       | 0.8%         |
| 3      | 8.0(5)   | -0.8               | 2.72(1)               | 0.014(2)                           | 2.57(1)               | 0.009(1)                       | 0.9%         |
| 4      | 8.3(6)   | -1.7               | 2.73(1).              | 0.007(1)                           | 2.59(1)               | 0.014(1)                       | 1.2%         |

("CN" is coordination number; " $\Delta E$ " is the energy difference between the experimental absorption energy and the calculated value in curve fitting; "D-W" is Debye Waller; "R factor" is the indication of the quality of curve fitting.)

#### 7.4.4 Chemisorption of CO

The numbers of exposed Pd active site of the reduced Pd/ZnO-CdSe samples are determined by the chemisorption uptake of CO with a Pd: CO = 1. The results are displayed in Table 7-5.

**Table 7-5** The number of exposed Pd atom ( $\mu\text{mol g}^{-1} \text{cat}^{-1}$ ) for a series of Pd/ZnO-CdSe samples.

| Sample                                                                       | 1<br>(0.0 wt% CdSe,<br>NZn=2.5) | 2<br>(9.4 wt% CdSe,<br>NZn=3.5) | 3<br>(19.2 wt% CdSe,<br>NZn=4.2) | 4<br>(26.4 wt% CdSe,<br>NZn=5.0) |
|------------------------------------------------------------------------------|---------------------------------|---------------------------------|----------------------------------|----------------------------------|
| Number of exposed<br>Pd atom ( $\mu\text{mol g}^{-1}$<br>$\text{cat}^{-1}$ ) | 55.3                            | 35.7                            | 25.8                             | 13.5                             |

Clearly, the number of exposed Pd atom decreases with the Zn decoration due to the blockage of some surface Pd atoms by Zn shell. The number of exposed Cu site in industry catalyst was measured by  $\text{N}_2\text{O}$  uptake and the value is  $520 \mu\text{mol g}^{-1} \text{cat}^{-1}$ .

## 7.5 Catalysis of a series of Pd/ZnO-CdSe samples in $\text{CO}_2$ hydrogenation

### 7.5.1 Catalysis procedure

The evaluation of catalytic ability of PdZn samples in  $\text{CO}_2$  hydrogenation was conducted in flow phase. The details are described in Chapter 3. Usually, the products include methanol, CO,  $\text{CH}_4$  and dimethylether (DME). However, in our system, the amounts of  $\text{CH}_4$  and DME produced are below the limit of detection. Thus, we only consider methanol and CO as the products of  $\text{CO}_2$  hydrogenation. The conversion, selectivity and carbon balance are calculated as follows:

$$\text{Conversion} = \frac{\text{Concentration of } (\text{CO}_2 \text{ before reaction} - \text{CO}_2 \text{ after reaction})}{\text{Concentration of CO}_2 \text{ before reaction}}$$

$$\text{Selectivity of methanol} = \frac{\text{Concentration of methanol}}{\text{Concentration of methanol} + \text{Concentration of CO}}$$

$$\text{Carbon balance} = \frac{\text{Concentrations of (methanol + CO + CO}_2 \text{ after reaction)}}{\text{Concentration of CO}_2 \text{ before reaction}}$$

### 7.5.2 Catalytic results

The plots of catalytic results of a series of Pd/ZnO-CdSe (5 wt% Pd) samples versus number of neighbour Zn atoms around Pd (derived from EXAFS) are summarized in Figure 7-7. The traditional Cu/ZnO based commercial catalyst (Cu ca. 50 wt%) was employed as a reference. According to Figure 7-7a and b, with various catalysts employed, methanol selectivity increases progressively with the concentration of Zn(0) in PdZn catalysts under a series of reaction conditions. For sample 4 (5 wt% Pd, 26.4 wt% CdSe) with the highest content of Zn(0) (NZn=5.0), methanol selectivity reaches 75 % at 4.5 MPa, 250 °C with WHSV (weight hourly space velocity) =18000 mL g<sup>-1</sup> h<sup>-1</sup>. Whereas for Cu-based commercial catalyst, the value is limited to 30% and 20% at 250°C and 270°C respectively due to the production of CO under the same condition. Meanwhile, as shown in in Figure 7-7c and d, we have evaluated the activities of Pd with Zn modifications (samples 1-4) in term of methanol weight time yields. For sample 4 (5 wt% Pd, 26.4 wt% CdSe), the values reached 12 and 6 g<sub>methanol</sub> g<sub>active metal</sub><sup>-1</sup> h<sup>-1</sup> at 4.5 and 2.0 MPa, 270°C, respectively (Fig. 4c,d). Comparing to the activities of employed Cu commercial catalyst (1.2 and 0.1 g<sub>methanol</sub> g<sub>active metal</sub><sup>-1</sup> h<sup>-1</sup>), they are 10-100 times higher than that of the Cu catalyst under the same conditions. Masahiro Saito has extensively reviewed the methanol productivities from CO<sub>2</sub>/H<sub>2</sub> over a wide range of Cu based catalysts under industrially applicable conditions. [12] The best reported activity is about 1.48 g<sub>methanol</sub> g<sub>active metal</sub><sup>-1</sup> h<sup>-1</sup> over 50%Cu/ZnO/Ga<sub>2</sub>O<sub>3</sub> at 250°C at 5 MPa, which are comparable in the same order of magnitude to our Cu commercial catalyst but is clearly less active than the Pd-based catalysts.

Taking the surface areas of Pd and Cu (numbers of active site per gram catalyst for Pd- and Cu-based catalysts are shown in Table 7-5) into account, the methanol TOF values are calculated and shown in Figure 7-8. The value for Pd increases dramatically with respect to the increasing Zn content and reaches  $3.3 \times 10^{-1} \text{ s}^{-1}$  at 4.5 MPa, 270 °C for sample 4 which is 80 fold of the methanol TOF for Cu in commercial catalyst. (Noted that the tested TOF of  $4.2 \times 10^{-3} \text{ s}^{-1}$  for Cu/ZnO commercial catalyst at 4.5 MPa, 270 °C agrees well with the reported value. [29]). Under the same temperature, the methanol TOF of Pd enriched with Zn at 2 MPa is  $1.9 \times 10^{-1} \text{ s}^{-1}$ , which is 350 times higher than that of the typical Cu catalyst under lower pressure condition. As far as we are aware, these values represent the highest values for various metal sites using a mixture of  $\text{H}_2:\text{CO}_2 \sim 3$ . This means, both the activity and selectivity of Pd for methanol synthesis are significantly promoted by the progressive Zn decoration.

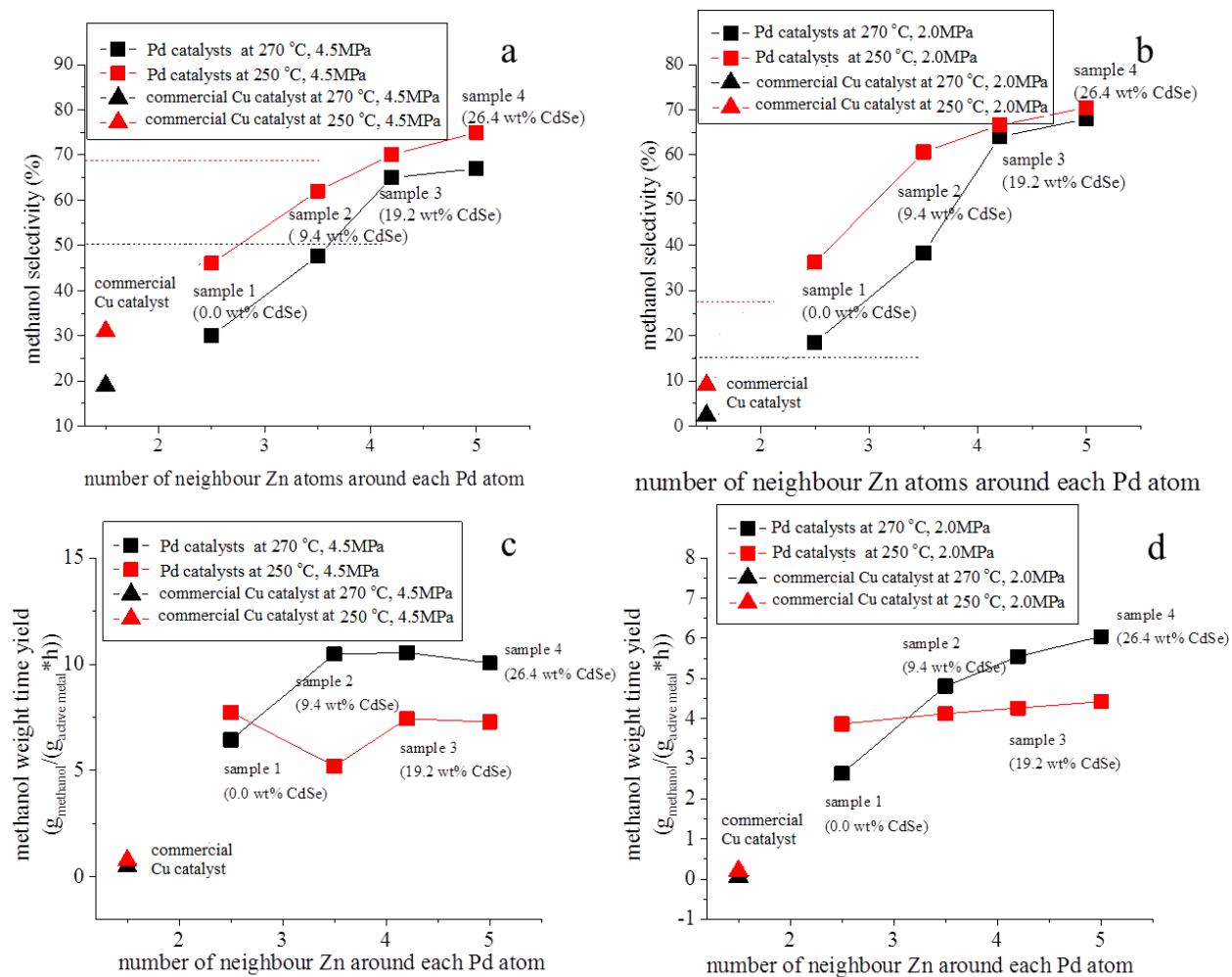


**Figure 7-7** The (a, b) methanol selectivity and (c, d) methanol weight time yield for a series of PdZn samples in CO<sub>2</sub> hydrogenation at (a, c) 4.5 MPa and (b, d) 2.0 MPa with WHSV= 18000 mL h<sup>-1</sup>g<sup>-1</sup>.

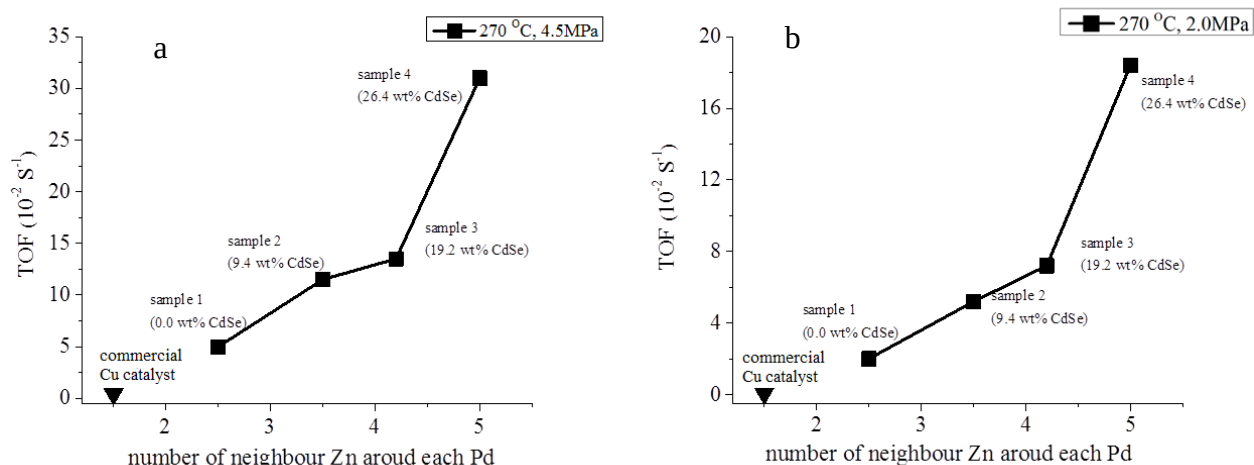


**Figure 7-8** The methanol TOF values of Pd in a series of Pd/ZnO-CdSe samples (5 wt% Pd) from CO<sub>2</sub> hydrogenation at (a) 4.5MPa and (b) 2.0 MPa, with WHSV=18000 mL h<sup>-1</sup>g<sup>-1</sup>, with reference to that of Cu in the commercial catalyst.

By comparing the results at 4.5 MPa to those at 2.0 MPa (Figure 7-7a, b), it is noted that methanol selectivity for the Cu commercial catalyst decreases sharply at lower pressure. The value is under 10% at 2 MPa (in a temperature range of 250-270 °C) which implies that the industry catalyst cannot work well at a low pressure as stated. In contrast, the methanol selectivities of the PdZn samples only decrease marginally especially for sample 4 (5 wt% Pd, 26.4 wt% CdSe) at lower reaction pressures. With the highest content of Zn, methanol selectivity was maintained at 70% (Figure 7-7b) with a decent activity (6 g<sub>methanol</sub> g<sub>active metal</sub><sup>-1</sup> h<sup>-1</sup>). Therefore, PdZn with a high content of Zn is a promising low-pressure catalyst for methanol synthesis from CO<sub>2</sub> hydrogenation.

To investigate the detailed catalytic behavior of catalysts under various pressures, a series of tests have been conducted at 250 °C. The results obtained from sample 4 (5 wt%, 26.4 wt% CdSe) and Cu-based commercial catalyst under different pressures are shown in Figure 7-9. For the

commercial catalyst, methanol selectivity decreases while CO selectivity rises at decreasing reaction pressure. All these results follow the trend of the values predicted by thermodynamic equilibrium (the dotted lines in Figure 7-9). This implies that the catalytic performance of Cu-based commercial catalyst is mainly guided by the thermodynamics. The relative higher selectivities for CO (lower selectivities for methanol) compared to thermodynamic data indicate a higher rate in RWGS than methanol synthesis until higher pressures >5 MPa are applied (Figure 7-9b). It is surprising to see that the methanol and CO selectivities over Pd@Zn surface (sample 4 (5 wt% Pd, 26.4 wt% CdSe)) do not follow the steep trends of thermodynamic values indicative of a strong kinetic control regime. Meanwhile, the observed methanol selectivities greatly exceed the thermodynamic values particularly at lower pressures, which suggest the unusual suppression of CO production from RWGS (Figure 7-9a). Compared with the Cu-based commercial catalyst, the catalytic performance of PdZn catalyst with high concentration of Zn is much more independent of the applied pressure.

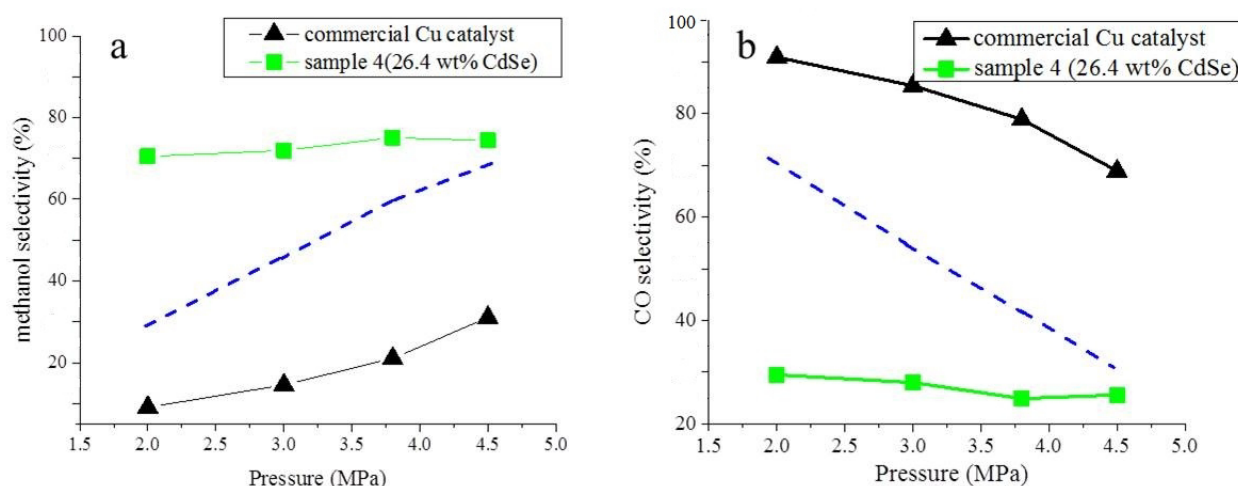


**Figure 7-9** The (a) methanol selectivity, (b) CO selectivity of sample 4 (5 wt% Pd, 26.4 wt% CdSe) and the Cu-based commercial catalyst at 250 °C under different pressures. (The blue dotted line indicates equilibrium values.)

The catalytic performances of PdZn catalysts (sample 1 (5 wt% Pd, 0.0 wt% CdSe), sample 4 (5 wt% Pd, 26.4 wt% CdSe)) and the Cu-based catalyst at 2.0 MPa at various temperatures are shown in Figure 7-10. For all the samples, methanol selectivity decreases with the raising temperature due to the effect of thermodynamics ( $\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$ ,  $\Delta H = -49.5 \text{ kJ mol}^{-1}$ ;  $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$ ,  $\Delta H = 41.2 \text{ kJ mol}^{-1}$ ). In a temperature range of 210 - 270 °C, the Pd-based catalysts show much higher methanol selectivity than Cu based commercial catalyst, particularly sample 4 with a high concentration of Zn(0) in PdZn bimetallic NPs.

The methanol yield of the Cu-based commercial catalyst decreases as temperature is increased from 210 to 270 °C. However, for sample 4 (5 wt% Pd, 26.4 wt% CdSe), the methanol yield rises sharply (Figure 7-10b) with increasing temperature through the activation of the catalyst, despite the low activity at temperature < 230 °C (Figure 7-10b). The methanol weight time yield of sample 4 reaches 20 times of the optimal value of Cu-based catalyst with much higher methanol

selectivity at 270 °C (Figure 7-10c). The methanol yield of sample 4 at 250~270 °C is higher than the theoretical value predicted at thermodynamic equilibrium condition when the RWGS reaction is taken into account. And it is approaching the new equilibrium value with no account for the RWGS reaction (Figure 7-10b). This implies the superior ability of PdZn which not only selectively catalyzes methanol synthesis, but also greatly suppresses the RWGS reaction.

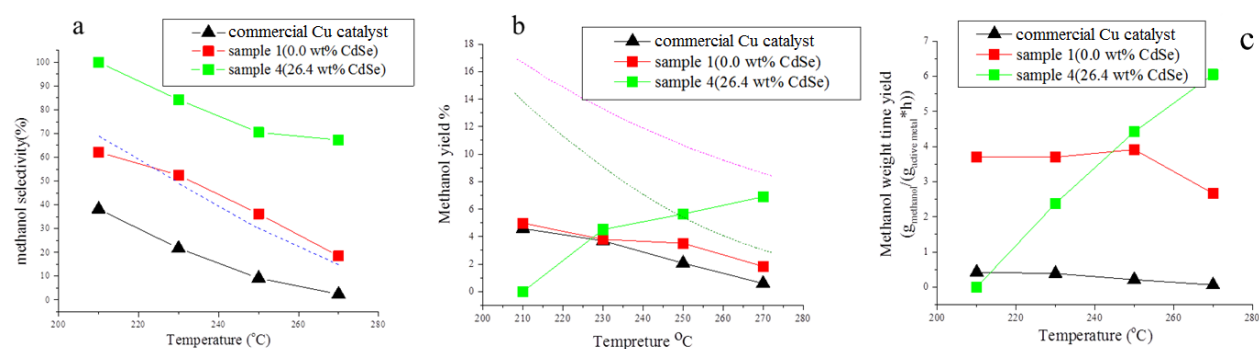


**Figure 7-10** (a) methanol selectivity, (b) methanol yield and (c) methanol weight time yield of the PdZn catalysts and the Cu-based commercial catalyst under 2.0 MPa pressure, at various temperatures (the blue dotted line in Figure 7-10a indicates the change of methanol selectivity at equilibrium condition with the temperature; the dotted lines in Figure 7-10b show the equilibrium methanol yields with (olive) and without (purple) taking the RWGS reaction into account.)

Based on the catalytic data under 2.0 MPa at various temperatures, the Arrhenius plots of RWGS on Cu-based commercial catalyst and sample 1 (5 wt% Pd, 0.0 wt% CdSe) sample 4 (5 wt% Pd, 26.4 wt% CdSe) are shown in Figure 7-11. The Arrhenius equation is described as:

$$\ln(k) = \ln(A) - \frac{\Delta E_a}{RT} \quad (\text{Equation 7-1})$$

where  $k$  is the reaction rate constant (here it is represented by TOF value),  $A$  is Arrhenius constant,  $\Delta E_a$  is the activation energy,  $R$  is the gas constant ( $=8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the

temperature.

The activation energies of RWGS are calculated to be 68.2 kJ mol<sup>-1</sup>, 70.5 kJ mol<sup>-1</sup> and 98.4 kJ mol<sup>-1</sup> for Cu-based catalyst, sample 1 (5 wt% Pd, 0.0 wt% CdSe) and sample 4 (5 wt% Pd, 26.4 wt% CdSe), respectively. The PdZn catalyst with low Zn content (sample 1) shows similar activation barrier to Cu-based catalyst for RWGS. By the decoration of a thicker Zn shell, the activation energy is significantly raised which confirms the kinetic suppression of RWGS on the PdZn surface.

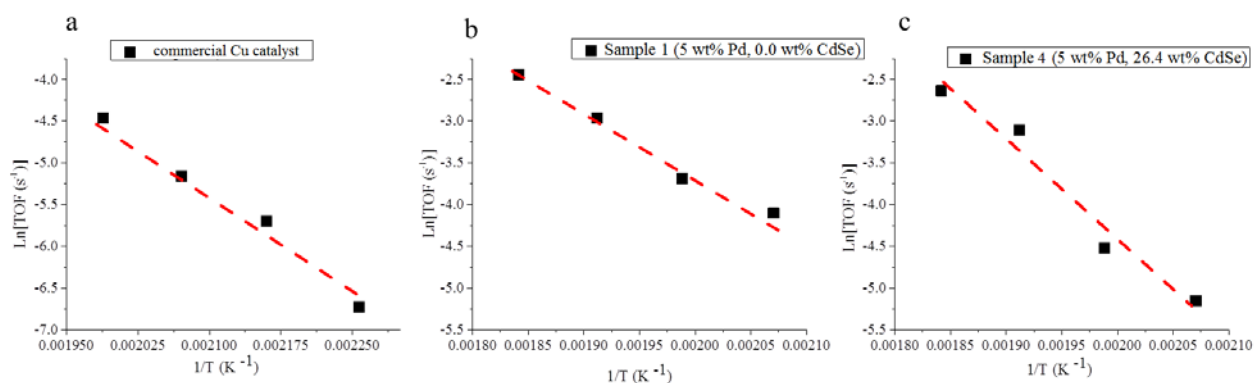
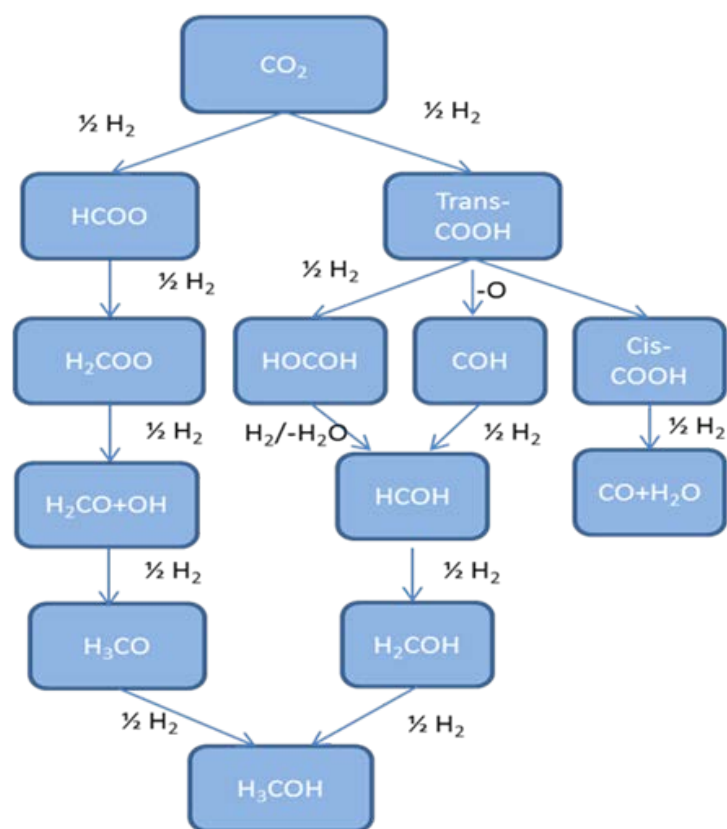


**Figure 7-11** The Arrhenius plots for RWGS on the (a) Cu-based commercial catalyst, (b) sample 1 (5 wt% Pd, 0.0 wt% CdSe) and (c) sample 4 (5 wt% Pd, 26.4 wt% CdSe).

## 7.6 Catalysis mechanism

Fourier transform infrared (FTIR) spectroscopy was employed to trace the catalytic mechanism of PdZn in CO<sub>2</sub> hydrogenation. A gas stream of 3 mol% CO<sub>2</sub> in H<sub>2</sub> was passed through the selected catalyst pellets (sample 1 (5 wt% Pd, 0.0 wt% CdSe,) and sample 4 (5 wt% Pd, 26.4 wt% CdSe)) which were pre-reduced in pure H<sub>2</sub> at 250 °C for 1 hour. The FTIR spectra were collected at various temperatures to observe the evolution of adsorbed intermediates on the catalyst surface.

For sample 1 (as shown in Figure 7-12a, c), a series of vibration bands including  $2000\text{ cm}^{-1}$ ,  $1800\text{ cm}^{-1}$ ,  $1595\text{ cm}^{-1}$ ,  $1395\text{ cm}^{-1}$ ,  $1230\text{ cm}^{-1}$ ,  $1502\text{ cm}^{-1}$ ,  $1702\text{ cm}^{-1}$  are observed. These IR peaks correspond to adsorbed CO (linear mode,  $2000\text{ cm}^{-1}$  and bridge mode,  $1800\text{ cm}^{-1}$ ), [29-31] formate ( $1595\text{ cm}^{-1}$ ,  $1395\text{ cm}^{-1}$ ), [32] dioxymethylene ( $1230\text{ cm}^{-1}$ ), [33,34] and formaldehyde ( $1502\text{ cm}^{-1}$ ,  $1702\text{ cm}^{-1}$ ) species on the surface. [35] The signals of formate was firstly detected at  $50\text{ }^{\circ}\text{C}$ . At elevated temperatures, the vibration bands for CO, dioxymethylene, formaldehyde become more intense (Figure 7-12c). It is generally believed that the first step of  $\text{CO}_2$  hydrogenation generates two different intermediates of HCOO and COOH (the IR vibration bands of COOH cannot be differentiated from those of HCOO due to the similar molecular structure). This leads to different reaction pathways as shown in Scheme 7-2. [36, 37] Further multi-step hydrogenation of HCOO produces methanol with dioxymethylene and formaldehyde species as intermediates while CO is the product from COOH decomposition. The increasing signals of CO with that of dioxymethylene, formaldehyde at elevated temperatures imply the parallel pathways for CO and methanol synthesis on sample 1 (5 wt% Pd, 0.0 wt% CdSe). However, for sample 4 (5 wt% Pd, 26.4 wt% CdSe) with a high content of Zn decoration, almost no CO signal was detected even at  $250\text{ }^{\circ}\text{C}$  (Figure 7-12b). But the signals for dioxymethylene and formaldehyde species also increase with rising temperature in the presence of adsorbed formate. This confirms the dramatic attenuation of CO production on the Zn rich PdZn surface. Consequently, methanol is observed as the main product on the surface of sample 4 (5 wt% Pd, 26.4 wt% CdSe). Additionally, with the consideration of RWGS, the methanol selectivity goes beyond the value predicted by the thermodynamic equilibrium.



**Scheme 7-2** The reported possible pathways in CO<sub>2</sub> hydrogenation.

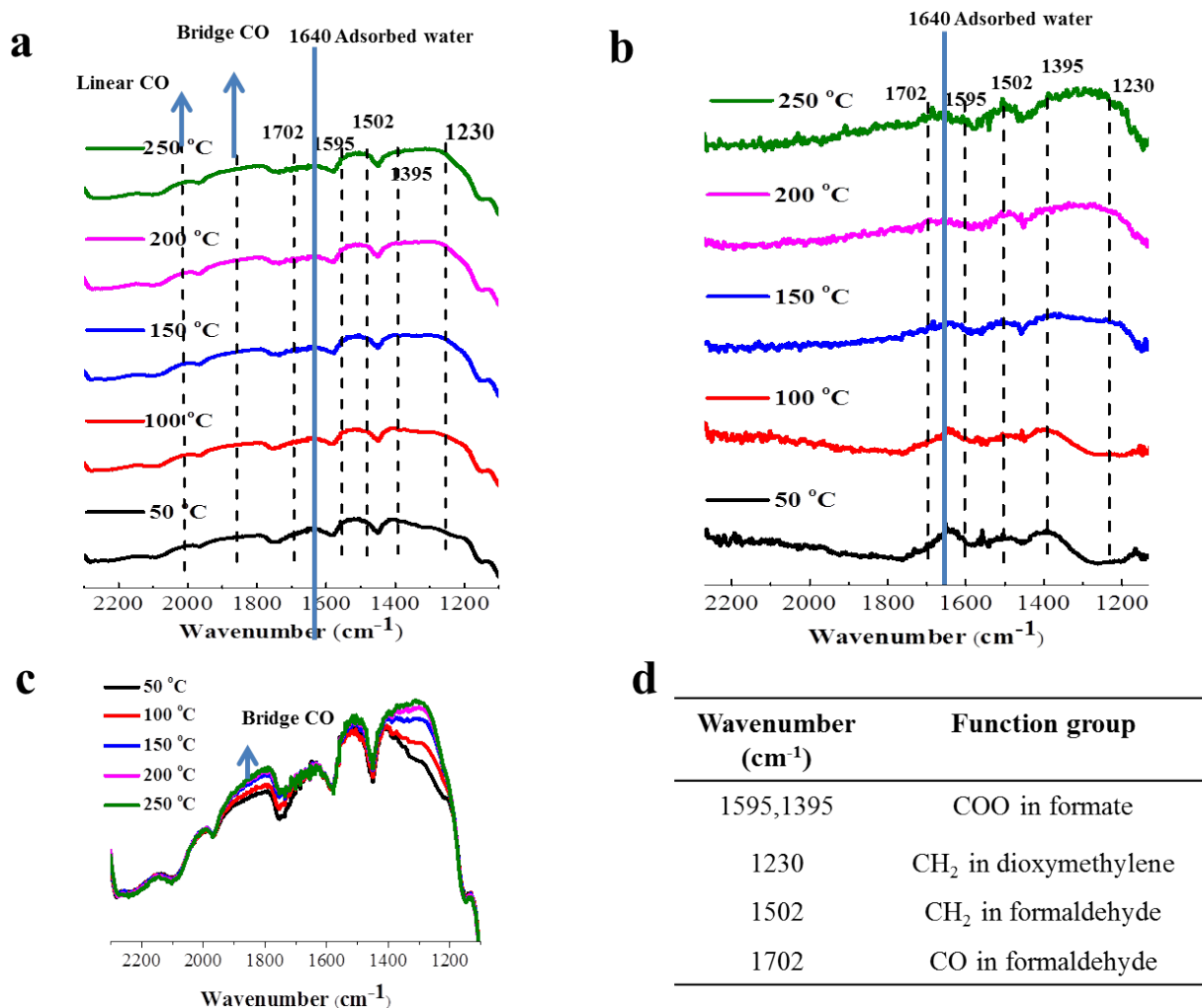


**Figure 7-12** FTIR spectra of adsorbed species on reduced (a) sample 1 (5 wt% Pd, 0.0 wt% CdSe) and (b) sample 4 (5 wt% Pd, 26.4 wt% CdSe) in CO<sub>2</sub> hydrogenation (3 mol% CO<sub>2</sub> in H<sub>2</sub> passes through a compressed pellet of 20 mg catalyst) at various temperatures; (c) the overlap of FTIR spectra for sample 1; (d) the assignment summary of the vibration bands in FTIR.

## 7.7 Modeling computation for PdZn surfaces

### 7.7.1 Computation method

The modeling calculations were finished with collaboration of Mr. Xinping Wu from East China

University of Science & Technology. PBE functional was used in the spin-polarized DFT calculations by using the Vienna *ab initio* Simulation Package (VASP).[38] The project-augmented wave (PAW) method was used to describe the interaction between atomic cores and electrons.[39] Wave functions were expanded in plane waves with an energy cutoff of 400 eV. For integrations over the Brillouin zone, we used a 5×5×1 Monkhorst-Pack grid for all calculations. The structure optimizations were converged until the Hellman-Feynman force on each ion was less than 0.02 eV Å<sup>-1</sup>. The calculated lattice parameter of bulk Pd was 3.95 Å, which is in good agreement with the values reported from previous studies. [40, 41]

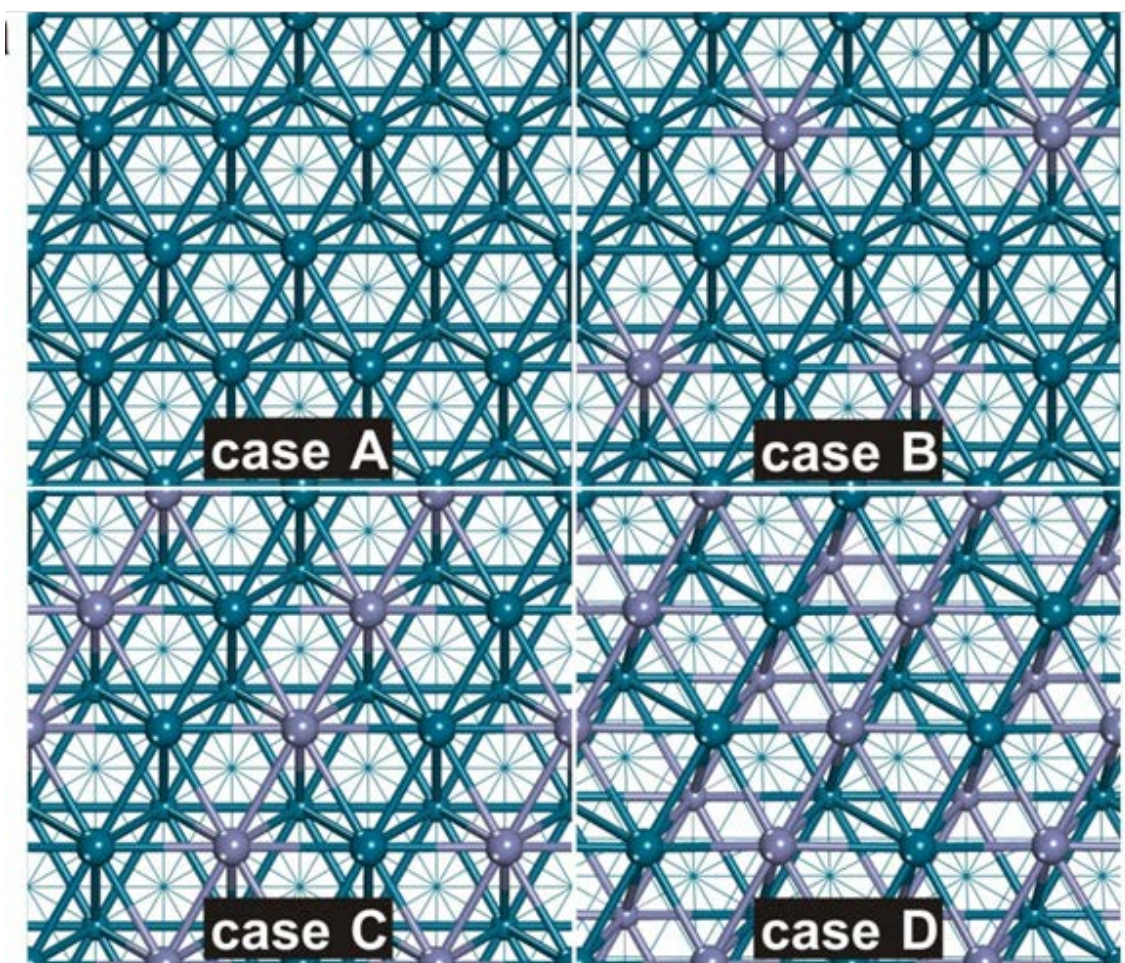
The Pd(111)-based surfaces were modeled by 4-layer slabs repeated in a 4×4 surface unit cell with the bottom one layer being fixed to the bulk parameters, while other layers were allowed to fully relax. To avoid interactions between slabs, all slabs were separated by a vacuum gap greater than 10 Å. Previous experimental studies suggested that the Zn atoms are contained entirely and distributed uniformly in the topmost layer of Pd(111) substrate after annealing when the Zn coverage is under 0.5 monolayer (ML).[42,43] For coverage nearing 0.5 ML, the p(2×1) PdZn (1:1) surface alloy is formed. Further increasing the Zn coverage will not break the (2×1) phase. Instead, Zn will infiltrate into the sub-surface layer first and then to the deeper layers. Accordingly, in this work, we constructed a p (2×2) 1ML-PdZn (3:1) surface alloy deposited Pd(111) (case B in Scheme 7-3) to represent the case of Zn coverage  $\sim$  0.25 ML. A p(2×1) 1ML-PdZn (1:1) surface alloy deposited Pd(111) (case C in Scheme 7-3) was then used to represent the case of Zn coverage  $\sim$  0.5 ML. To describe the case of high Zn coverage ( $\sim$  1 ML), a p(2×1) 2ML-PdZn (1:1) surface alloy deposited Pd (111) (case D in Scheme 7-3), which was regarded to be more stable than the case C, was constructed.[44]

The binding energy (BE) of an adsorbate to the substrate is calculated as follows:

$$BE = E_{\text{ad}} + E_{\text{sub}} - E_{\text{ad/sub}}$$

where  $E_{\text{ad}}$ ,  $E_{\text{sub}}$  and  $E_{\text{ad/sub}}$  are the DFT calculated total energies of the gas-phase adsorbate, clean substrate and adsorption complex, respectively.

Transition states were located by using the climbing-image nudged elastic band (CI-NEB) method. [45-47]



**Scheme 7-3** Zn decorated Pd(111) surfaces of cases A-D at Zn coverages of 0.00, 0.25, 0.50 and 1.00 monolayer (ML), respectively. Pd and Zn atoms are in cyan and purple, respectively. The bigger and smaller balls represent the first and second layer atoms, respectively.

### 7.7.2 Computation results

The electronic structures of Pd cases A-D with various Zn content were calculated (Figure 7-13). The density of states diagrams for Pd cases A→D are displayed in Figure 7-14. Comparing the diagram of pure Pd(111) with other Pd-based surfaces, a localized narrow band at low energies is observed to replace the states at the Fermi-edge which is indicative of the strong Pd-Zn covalent bonds. The difference in electronegativity between Zn (1.65) and Pd (2.2) implies that the Pd

atoms in PdZn should get negative charge from neighbour Zn atoms through the bonding interaction of Pd and Zn. As shown in Figure 7-13, the *d*-band filling of PdZn rises with increasing content of Zn, which confirms the charge transfer from Zn to Pd. This strong interaction of Pd-Zn also reduces the *d*-band center of PdZn bimetallic phase. As shown in Figure 7-13b, the *d*-band center position decreases with the increasing decoration of Zn.

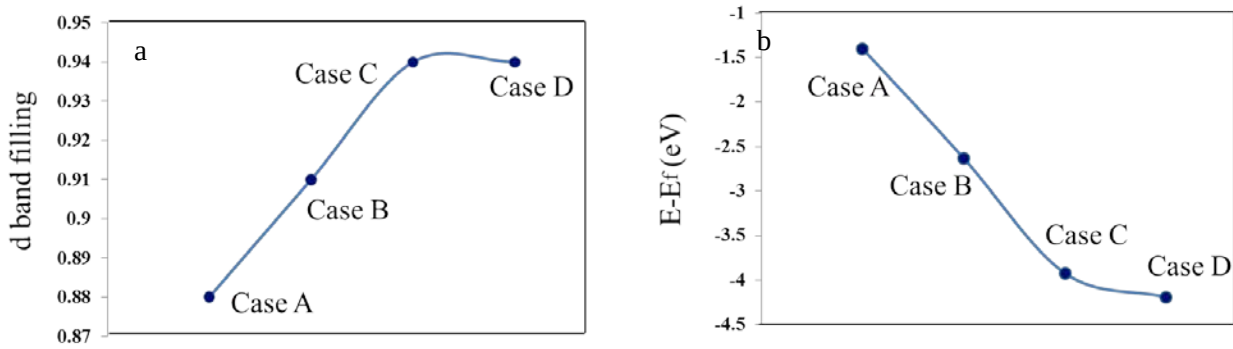


**Figure 7-13** (a) The calculated *d*-band fillings and (b) *d*-band center position of top surface atoms for Pd cases A-D.

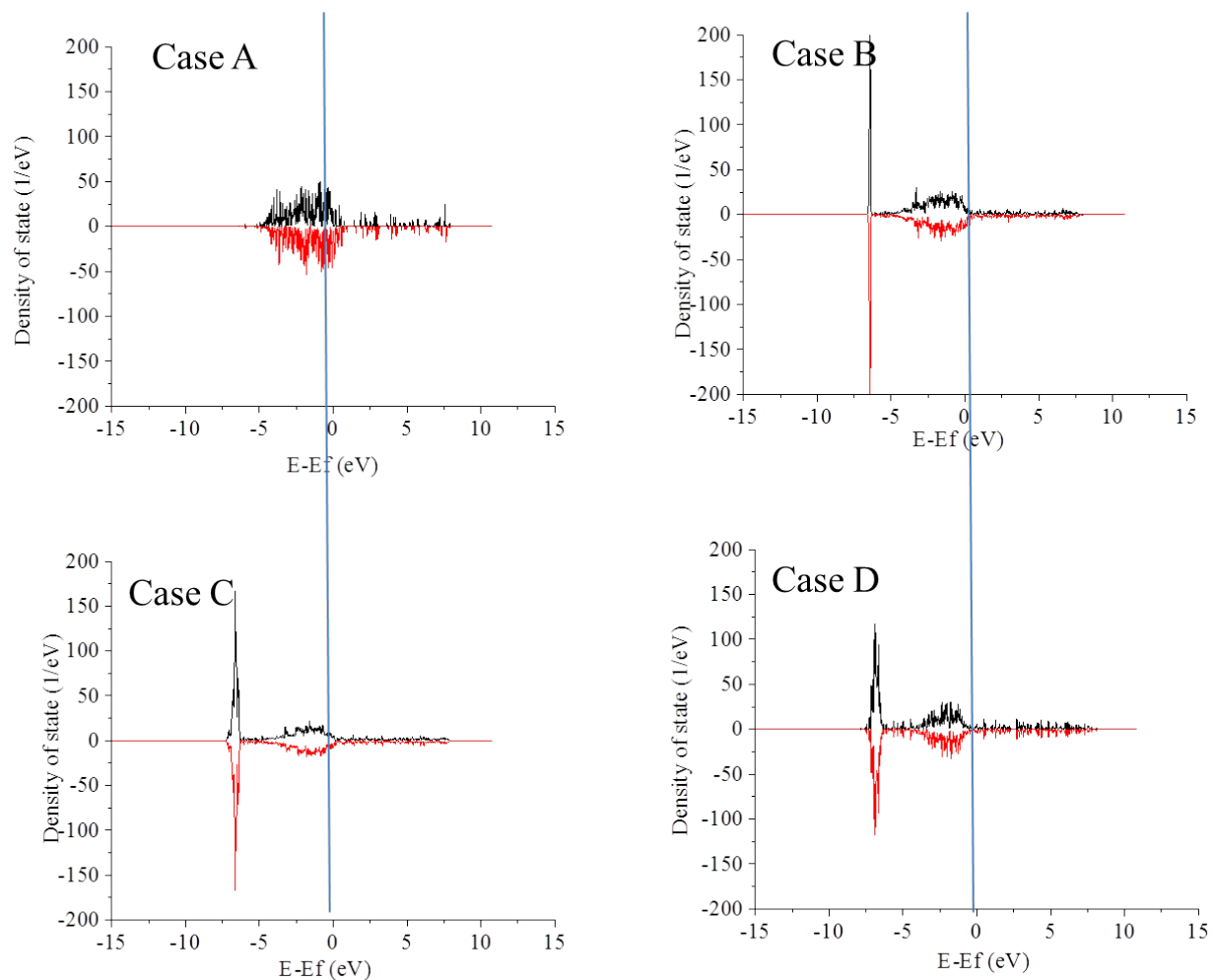


**Figure 7-14** The calculated density of states (DOS) for the surface atoms of Pd cases A-D.

It is well understood that the varied *d*-band structure of active site influences the interaction with reactants or intermediates in catalysis. Given that HCOO and COOH are considered as the precursors for methanol and CO, the adsorption of HCOO and COOH on Pd cases A-D is thoroughly investigated. As shown in Figure 7-15a, the potential energy difference of HCOO\* and COOH\* states (in term of  $E_{\text{HCOO}^*} - E_{\text{COOH}^*}$ , \* indicates adsorbed species) at pure Pd(111) surface (case A) is +0.18 eV. This positive value implies the relatively higher stability of adsorbed COOH than that of HCOO on pure Pd surface. Meanwhile, as shown Figure 7-15b, the

barrier of CO<sub>2</sub> hydrogenation to COOH (1.21 eV) is lower than that of HCOO formation (1.49 eV). Both calculated values indicate that the production of COOH is more favourable than that of HCOO at pure Pd(111) surface from the perspectives of thermodynamics ( $E_{\text{HCOO}^*} - E_{\text{COOH}^*}$ ) and kinetics (activation barrier). However, with the growing decoration of Zn from case A to case D, The potential energy difference of the two ( $E_{\text{HCOO}^*} - E_{\text{COOH}^*}$ ) reverses gradually from +0.18 eV (case A) to -0.09 eV (case B), -0.22 eV (case C) and reaching -0.70 eV in case D. Simultaneously, the activation barrier of HCOO formation decreases with Zn concentration as 1.49→1.25→1.08→0.92 eV, while that of COOH formation shows the opposite trend as 1.21→1.33→1.36→1.44 eV, from case A to D, respectively. This means the production of HCOO replaces that of COOH as the preferred reaction route in the first step of CO<sub>2</sub> hydrogenation with progressive Zn decoration on Pd surfaces. As a result, the selectivity of methanol synthesis with HCOO as the intermediate gets promoted at increasing Zn content in the PdZn catalyst.

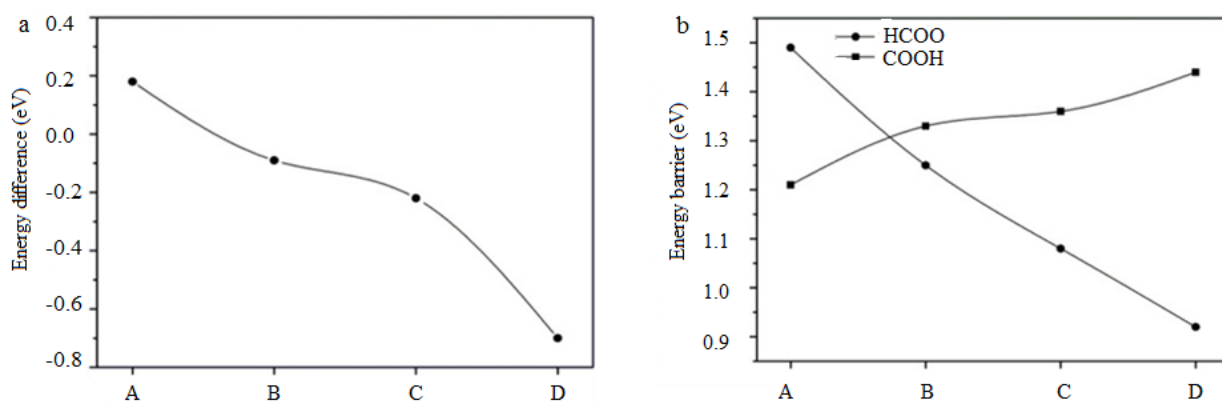


**Figure 7-15** (a) the difference of potential energy in adsorbed HCOO and COOH in term of  $E_{\text{HCOO}^*} - E_{\text{COOH}^*}$  on Pd cases A→D; (b) the activation barrier of HCOO formation and COOH formation from CO<sub>2</sub> hydrogenation on Pd cases A→D.

The potential energy surfaces of CO<sub>2</sub> hydrogenation on cases A and D are shown in Figure 7-16. The profile of HCOO formation lies over that of COOH formation in the first step of CO<sub>2</sub> hydrogenation on pure Pd (111). In contrast, with 2 ML PdZn (1:1) (case D, 1ML Zn coverage) the energy surface for the route of producing HCOO lowers significantly and eventually locates under that of COOH formation. This calculated result directly demonstrates the variation of catalytic reaction route from COOH formation to HCOO formation on Pd-based surface by the decoration of Zn. Meanwhile, the calculation of the further transformations of COOH is also displayed. The decomposition to CO is the most favourable reaction route with lowest activation barrier among the three possible pathways, which confirms the rapid CO production from COOH. And once the formation of trans-COOH is suppressed, CO production would be inhibited.

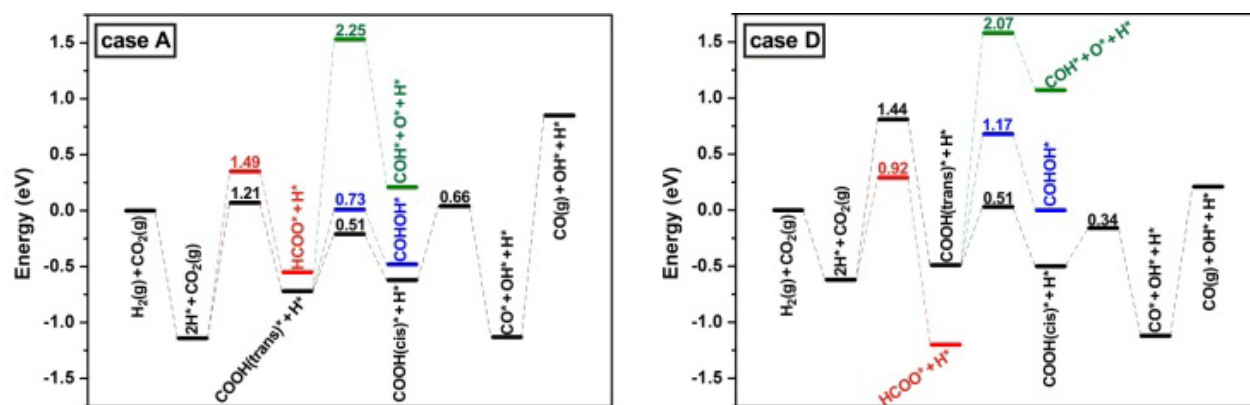


**Figure 7-16** The calculated reaction pathways of CO<sub>2</sub> hydrogenation at cases A (pure Pd(111)) and D (2ML-PdZn (1:1) surface alloy deposited Pd(111)). The Numbers labeled in the figure are in unit of eV representing the corresponding reaction barriers. \* represents adsorbed species. (Note that there is an equilibrium between trans-COOH and cis-COOH isomer pair existing on the catalyst surface and the COOH mentioned in the text refers to trans-COOH.)

The lowest unoccupied molecular orbitals (LUMO) for HCOO and COOH are shown in Figure

7-17. Clearly, for HCOO, the two large lobes of orbital are mainly distributed on the two O atoms, which indicate HCOO is adsorbed on catalyst surface through the two oxygen atoms with high electron affinity. With the decoration of Zn, the upshifted *d*-band fillings enhance the  $\pi$  electron donation from Pd-based surfaces to the two oxygen atoms and further stabilize the HCOO species. Thereby, the binding energies of HCOO on various PdZn surfaces increase from cases A to D as shown in Figure 7-18. For COOH, it interacts with Pd through the C-O group as indicated by the location of the two large orbital lobes (Figure 7-17b) on C=O group which is lower in electron affinity than the two oxygen atoms in HCOO. Thereby, COOH is less sensitive to the electron density change on Pd-based surface, and the binding energies of COOH from cases A to D remain almost constant (Figure 7-18). Consequently, with the progressive increase of Zn content, the PdZn surface stabilizes the HCOO species selectively rather than COOH and leads to an excellent methanol selectivity.

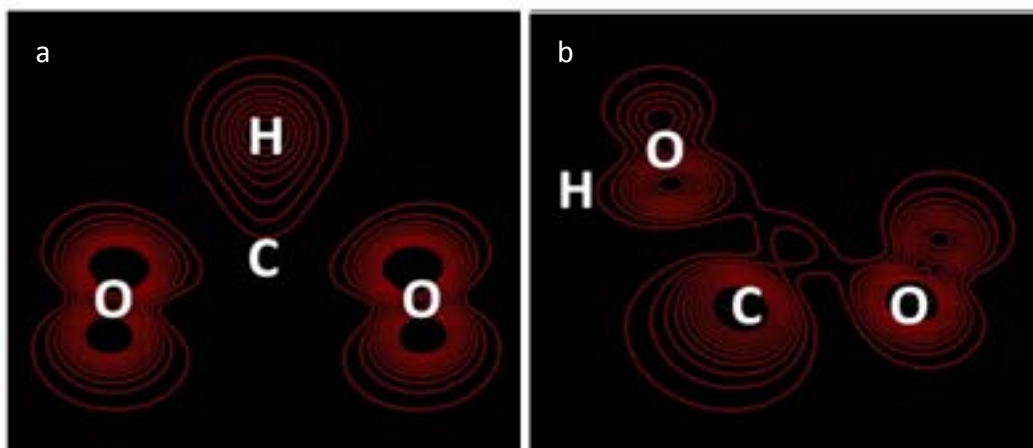


**Figure 7-17** The calculated LUMO contours of (a) HCOO and (b) COOH species.

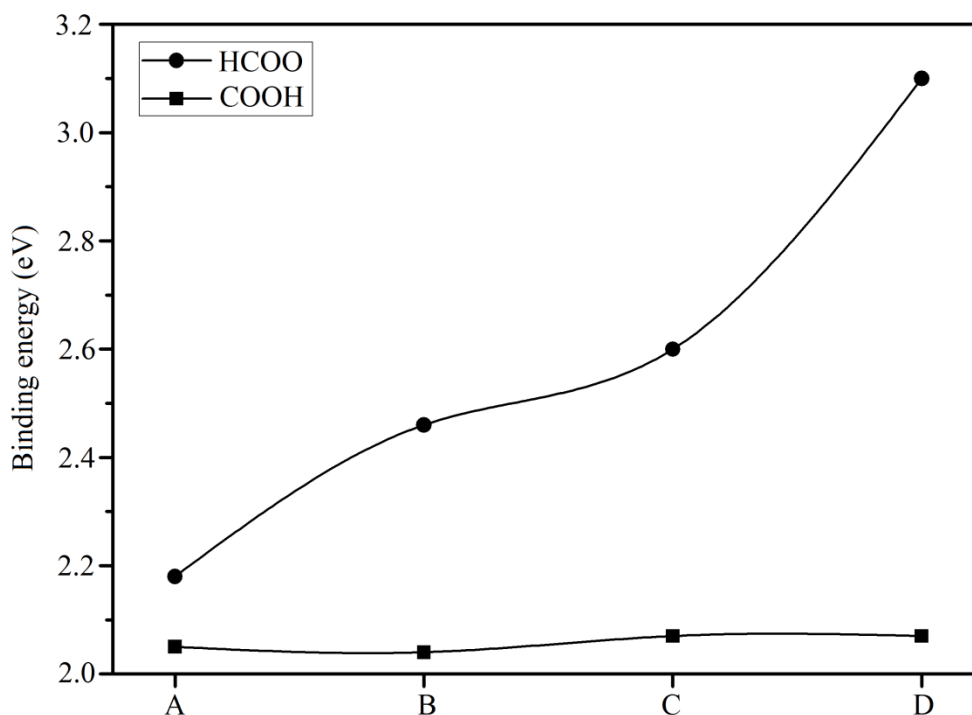


**Figure 7-18** Binding energies of HCOO and COOH species at cases A-D.

## 7.8 The comparison of Pd-based and Cu-based systems with high Zn content

### 7.8.1 Synthesis of Zn rich CuZn bimetallic NPs

To systematically investigate the influence of Zn decoration on both Cu and Pd system, a Zn rich CuZn catalyst was also synthesized to compare with the PdZn catalyst.

The enrichment of Zn(0) in the Cu-based catalyst was achieved by the incorporation of Ga into Cu/ZnO system, which promoted the reduction of ZnO to Zn(0). The synthesis of Cu/ZnGaO<sub>x</sub> is described as follows:

Cu/ZnGaO<sub>x</sub> catalyst was synthesized using a pH-controlled co-precipitation method. The metal precursors were hydrated metal nitrate salts from Aldrich: Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and Ga(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O. For a typical preparation condition, the metal nitrates [3.14 g Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O;

4.64g  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ; 0.63g  $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ] were dissolved in 100 mL deionized water. The  $\text{Na}_2\text{CO}_3$  aqueous solution was prepared by dissolving 3.50 g of  $\text{Na}_2\text{CO}_3$  in 100 mL DI water. A delivery pump with two 50 mL syringes was used to inject the precursor metal nitrate solution and the  $\text{Na}_2\text{CO}_3$  solution at constant rates of  $0.42 \text{ mL min}^{-1}$  and  $0.5 \text{ mL min}^{-1}$ , respectively, in an automatic and reproducible manner. The solutions were added simultaneously into a plastic reactor containing 250 mL of pre-heated DI water with magnetic stirring at 1000 rpm. The pH of the precipitating solution was carefully maintained at 6.5 with an error range of  $\pm 0.1$  (a temperature-dependent pH meter was used to monitor the pH). The precipitation temperature was set at  $80^\circ\text{C}$ . The resulting precipitate was kept in solution at  $100^\circ\text{C}$  for 15 hours. After aging, the precipitate was collected by centrifugation at 6500 rpm, which was then washed with DI water extensively to remove residual  $\text{Na}^+$  ions. The harvested product was dried in air at  $80^\circ\text{C}$  overnight and then calcined at  $380^\circ\text{C}$  in static air for 3 hours to produce the final catalyst. The pre-reduction of the catalyst was carried out in pure  $\text{H}_2$  atmosphere with a flow rate of  $20 \text{ sccm}$ . The incorporation of Ga into the Cu/ZnO system promotes the reduction of ZnO to Zn, resulting in a higher ratio of Zn(0):Cu(0) in Cu/ZnGaO<sub>x</sub> catalyst than that in Cu/ZnO as depicted by the XPS results as shown in Table 7-6.

**Table 7-6** The integration results of XPS for Cu/ZnO and Cu/ZnGaO<sub>x</sub>.

| Sample                | Chemical Composition<br>of Cu:Zn:Ga | Zn(0)/(Zn(0)+Zn(II)) | Zn(0)/Cu(0) |
|-----------------------|-------------------------------------|----------------------|-------------|
| Cu/ZnO                | 43: 57: 0                           | 0.19                 | 0.66        |
| Cu/ZnGaO <sub>x</sub> | 43: 52: 5                           | 0.32                 | 1.32        |

### 7.8.2 Catalytic performance of Zn rich Cu-based catalyst

The catalytic results of Cu/ZnGaO<sub>x</sub> at 250 °C under various pressures are summarized in Table 7-7.

**Table 7-7** The catalytic performance of Cu/ZnGaO<sub>x</sub> catalyst under various pressures at 250 °C (0.1 g catalyst, 30 stp mL min<sup>-1</sup> flow rate, CO<sub>2</sub>:H<sub>2</sub> = 1:2.8)

| Pressure (MPa) | Conversion (%) | S <sup>a</sup> methanol (%) | S <sup>a</sup> CO (%) | Carbon balance |
|----------------|----------------|-----------------------------|-----------------------|----------------|
| 4.5            | 26.5           | 43.5                        | 56.5                  | 98.2           |
| 3.8            | 18.2           | 12.2                        | 87.8                  | 99.3           |
| 3.0            | 17.4           | 8.3                         | 91.7                  | 100.1          |
| 2.0            | 17.4           | 4.2                         | 95.8                  | 100.2          |

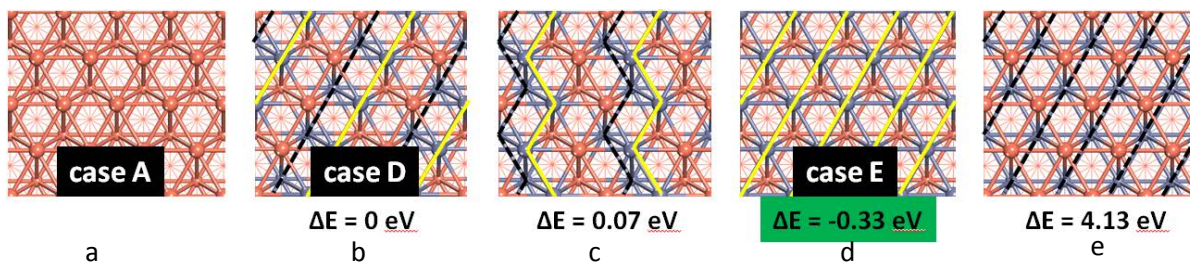
(<sup>a</sup>“S” is the abbreviation of selectivity.)

The methanol selectivities of this supported Zn rich CuZn catalyst are much lower than those of Pd@Zn bimetallic catalysts under a wide range of pressures. Comparing to the commercial Cu/ZnO catalyst (methanol selectivity is around 30%), the extra Zn(0) enrichment in our Cu-based catalyst enhances the methanol selectivity to 43.5 % at 4.5 MPa but the value drops sharply with the decreasing pressure. This implies that Zn decoration on Cu-based catalysts cannot stop the descending trend of methanol selectivity against the decreasing pressure, which is distinctly different from PdZn system (sample 4 (5 wt% Pd, 26.4 wt% CdSe)).

### 7.8.3 Modeling computation

DFT calculation was employed to investigate the catalytic properties of CuZn surface. The results of pure Cu (111) (case A) and Cu(111) with 1 ML coverage of Zn (Case D, Case E) are selected to compare with PdZn surfaces. Case E with 1 ML Zn deposited Cu(111) is the most stable configuration of a given composition according to our stability analyses (see scheme 7-4), and is 0.33 eV more stable in total energy than case D. Given the fact that case D has the similar

geometric structures with the corresponding PdZn case, it was also taken into consideration in this work.



**Scheme 7-4** The calculated structures of Cu-based catalysts; (a) Cu (111), (b-e) various configurations of 1 ML Zn decoration on Cu(111). Cu and Zn atoms are in brown and purple, respectively. The bigger and smaller balls represent the first and second layer atoms, respectively. The yellow line indicates the surface Zn atom distribution on Cu(111). Case D and case E are labelled and selected to compare with PdZn surfaces due to the lower energies than other ones

The calculated *d*-band structures of Cu-based surfaces and their comparison with that of Pd-based surfaces are displayed in Table 7-8.

**Table 7-8** The influence of Zn decoration on the electronic structure of the CuZn surfaces.

| Surface         | Case                                                 | <i>d</i> -band center<br>(eV) | Surface <i>d</i> -band filling |
|-----------------|------------------------------------------------------|-------------------------------|--------------------------------|
| <b>Cu-based</b> | A<br>(Cu(111))                                       | -1.95                         | 0.94                           |
|                 | D<br>(2 ML Cu <sub>1</sub> Zn <sub>1</sub> /Cu(111)) | -4.48                         | 0.95                           |
|                 | E<br>(1 ML Zn/Cu(111))                               | -6.79                         | 0.96                           |
| <b>Pd-based</b> | A<br>(Pd(111))                                       | -1.40                         | 0.89                           |
|                 | D<br>(2 ML Pd <sub>1</sub> Zn <sub>1</sub> /Pd(111)) | -4.19                         | 0.94                           |

As shown in Table 7-8, Zn decoration shows similar effects on Cu and Pd-based surfaces: downshifting the *d*-band center position and increasing the *d*-band filling, which is indicative of the charge transfer from Zn to Pd or Cu. But the variation is more significant in Pd-based system than in Cu-based system due to the larger difference in electronic configuration between Pd ( $4d^{10}5s^0$ ) and Zn ( $3d^{10}4s^2$ ) than that between Cu ( $3d^{10}4s^1$ ) and Zn ( $3d^{10}4s^2$ ).

Various electronic configurations of metal surfaces usually lead to different adsorptivities. The calculated H adsorption energies and the energy differences of HCOO\* and COOH\* species (in terms of  $E_{\text{HCOO}^*} - E_{\text{COOH}^*}$ ) on both Pd-based and Cu-based surfaces are shown in Table 7-9.

**Table 7-9** The calculated H adsorption energies and the potential energy differences of HCOO\* and COOH\* species on Cu-based and Pd-based surfaces.

| Surface         | Case                                                 | H adsorption energy<br>(eV) | $E_{\text{HCOO}^*} - E_{\text{COOH}^*}$<br>(eV) |
|-----------------|------------------------------------------------------|-----------------------------|-------------------------------------------------|
| <b>Cu-based</b> | A<br>(Cu(111))                                       | 0.16                        | -0.79                                           |
|                 | D<br>(2 ML Cu <sub>1</sub> Zn <sub>1</sub> /Cu(111)) | 0.06                        | -0.80                                           |
|                 | E<br>(1 ML Zn/Cu(111))                               | -0.50                       | -1.11                                           |
| <b>Pd-based</b> | A<br>(Pd(111))                                       | 0.57                        | +0.18                                           |
|                 | D<br>(2 ML Pd <sub>1</sub> Zn <sub>1</sub> /Pd(111)) | 0.31                        | -0.70                                           |

As shown in Table 7-9, the values of the energy differences of HCOO\* and COOH\* ( $E_{\text{HCOO}^*} - E_{\text{COOH}^*}$ ) species on the Cu-based surfaces are negative (-0.79, -0.80 and -1.11 eV for case A, case D and case E, respectively). This indicates that the formation of HCOO\* is favoured than that of COOH\* on Cu-based surfaces. And the decoration of Zn further enhances the HCOO\* production in the first step of CO<sub>2</sub> hydrogenation. However, as implied by the low H adsorption energies (0.16, 0.06 and -0.50 eV for case A, case D and case E, respectively), Cu-based surfaces exhibit very low activity in dissociating H<sub>2</sub> into atomic H. This leads to a low coverage of surface H and slows down the further hydrogenation of HCOO\* to methanol. On the other hand, the decomposition of COOH\* to CO\* and OH\* is independent of the concentration of surface H. As depicted in Figure 7-16, the produced COOH\* in the first step can be consumed rapidly and this shifts the equilibrium between HCOO\*/COOH\* towards COOH formation. Thus, no

significant specificity for methanol production over CO production was observed in Cu-based system despite the negative value of  $E_{\text{HCOO}^*} - E_{\text{COOH}^*}$ . The methanol selectivities for all the Cu-based catalysts are below 50%. Besides the activity of the catalyst, the reaction pressure also influences the surface coverage of atomic H. At 4.5 MPa, with a decent coverage level of surface H due to the high reaction pressure, the methanol selectivity of Cu/ZnGaO<sub>x</sub> is even enhanced comparing with Cu/ZnO, owing to the promoted HCOO\* formation in the first step of CO<sub>2</sub> hydrogenation by the extra Zn decoration. But with lowering reaction pressure, the concentration of atomic H on Cu catalyst is not high enough to afford sufficient hydrogenation of HCOO\* to methanol. As shown in Table 7-9, the H adsorption energy is further reduced by Zn decoration on case D and case E, which limits the surface H coverage and restricts methanol production. Thus, the high content of Zn shows no enhancement on the dropping of methanol selectivity against the decreasing pressure despite the initial selective formation of HCOO\* on Cu-based catalyst. In contrast, Pd surfaces shows superior ability to Cu surfaces in activating H<sub>2</sub> as indicated by the H adsorption energy (0.57 and 0.31 eV for case A and case D, respectively). The high coverage of atomic H promotes methanol production upon the formation of HCOO\* even under low pressure as 2 MPa. Although the decoration of Zn also reduces the H adsorption on Pd-based surfaces, it enhances the selective formation of HCOO\* in the first step of CO<sub>2</sub> hydrogenation and also promotes the migration of H on the surface. As a result, methanol selectivity was uniquely strengthened with the increasing Zn content at Pd-based surface.

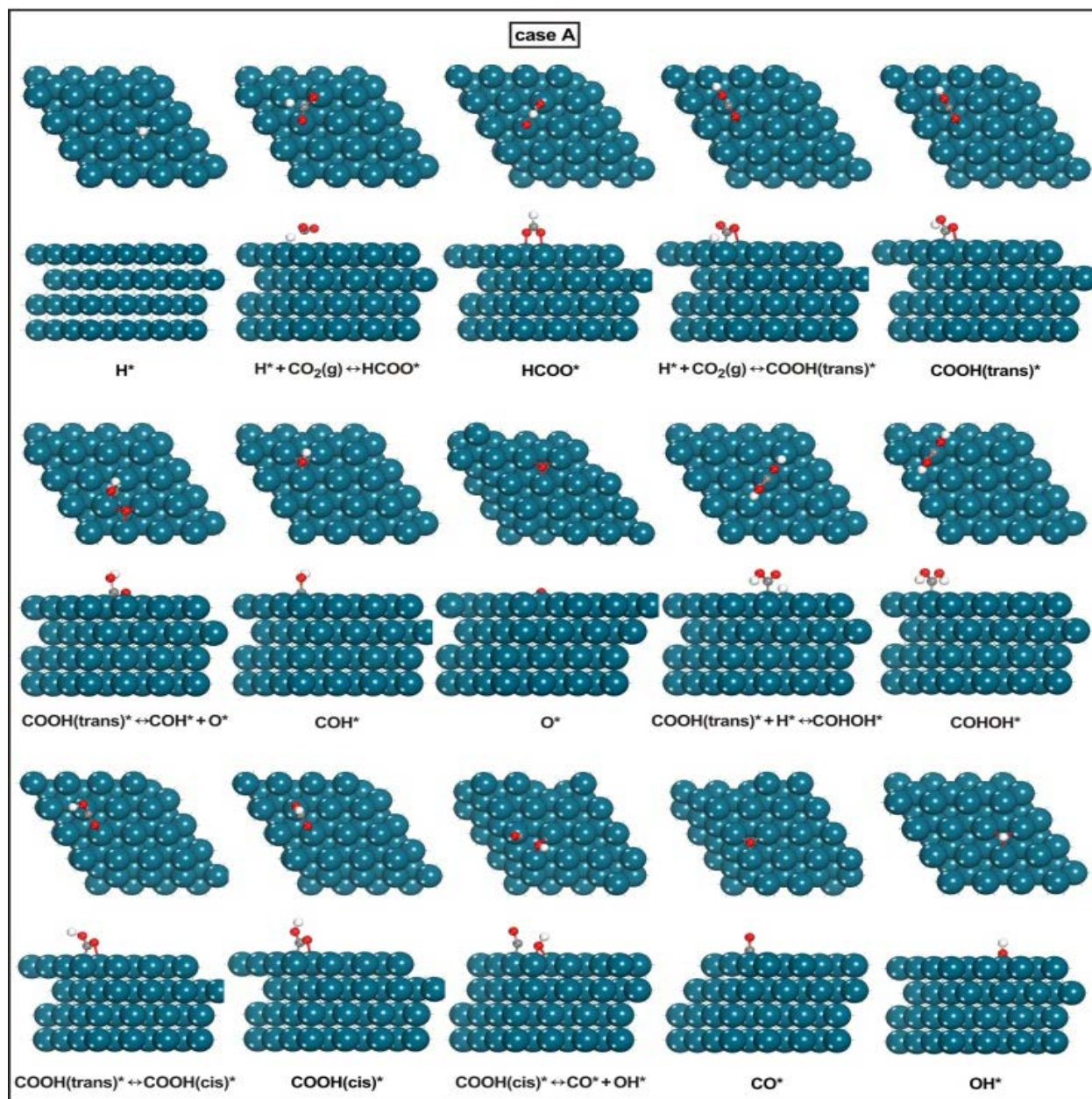
## 7.9 Conclusion

A series of Pd@Zn core-shell bimetallic catalysts with different compositions were prepared successfully through the decoration of Pd by reactive Zn atoms from the controllable reduction of the underneath ZnO-CdSe support. The thickness of the Zn shell depends on the ratio of ZnO:

CdSe in the support. In CO<sub>2</sub> hydrogenation, the Zn decoration not only strongly enhances the methanol production (the TOF on Pd reaching  $3.3 \times 10^{-1} \text{ s}^{-1}$ ), but also suppresses the CO production from RWGS reaction. This makes the methanol selectivity independent of the reaction pressure, remaining at 70% even at 2.0 MPa. The excellent catalytic property is ascribed to (i) the high electron density on PdZn phase, which stabilizes HCOO (the intermediate to methanol) selectively rather than COOH (the precursor of CO); and (ii) its high activity in dissociating H<sub>2</sub>, which sufficiently converts HCOO into methanol. With the increasing demand for green chemical synthesis, the outstanding catalytic performance (70% methanol selectivity,  $1.9 \times 10^{-1} \text{ s}^{-1}$  TOF at 2 MPa) of this novel Pd-based catalyst provides a promising route for methanol production from the conversion of biomass generated CO<sub>2</sub>/H<sub>2</sub> gas without further pressurisation. The whole process is renewable, energy efficient and cost efficient.

## Appendix

The corresponding structures of the adsorbed species in the calculations are summarized in Figure 7-19 and Figure 7-20.



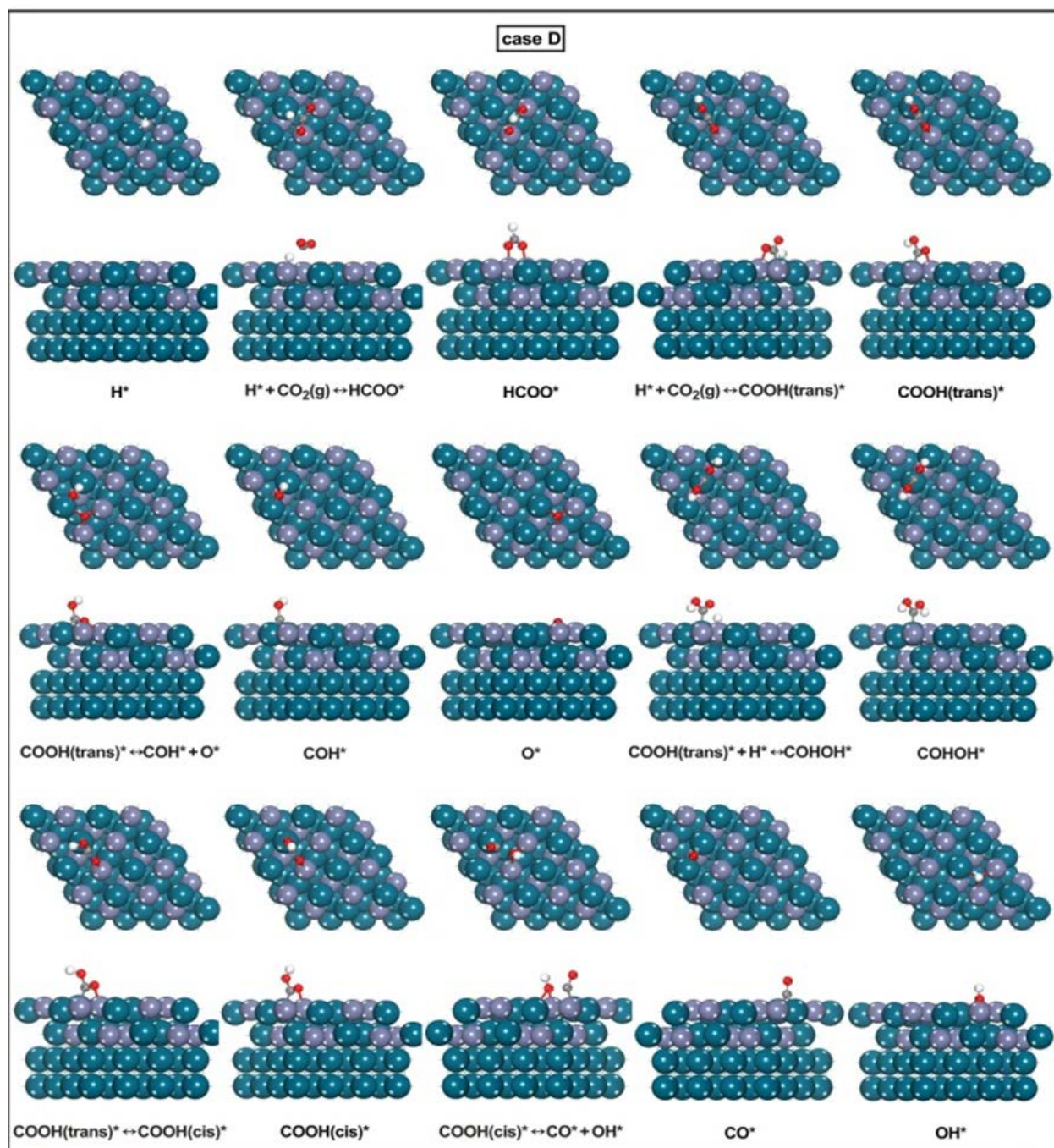


**Figure 7-19** Corresponding structures of adsorbed species shown in Figure 7-16. Pd, Zn, H, C and O atoms are in cyan, purple, white, grey and red, respectively. Note: COOH\* reported in the main text represents the COOH (trans)\* species in the calculation.

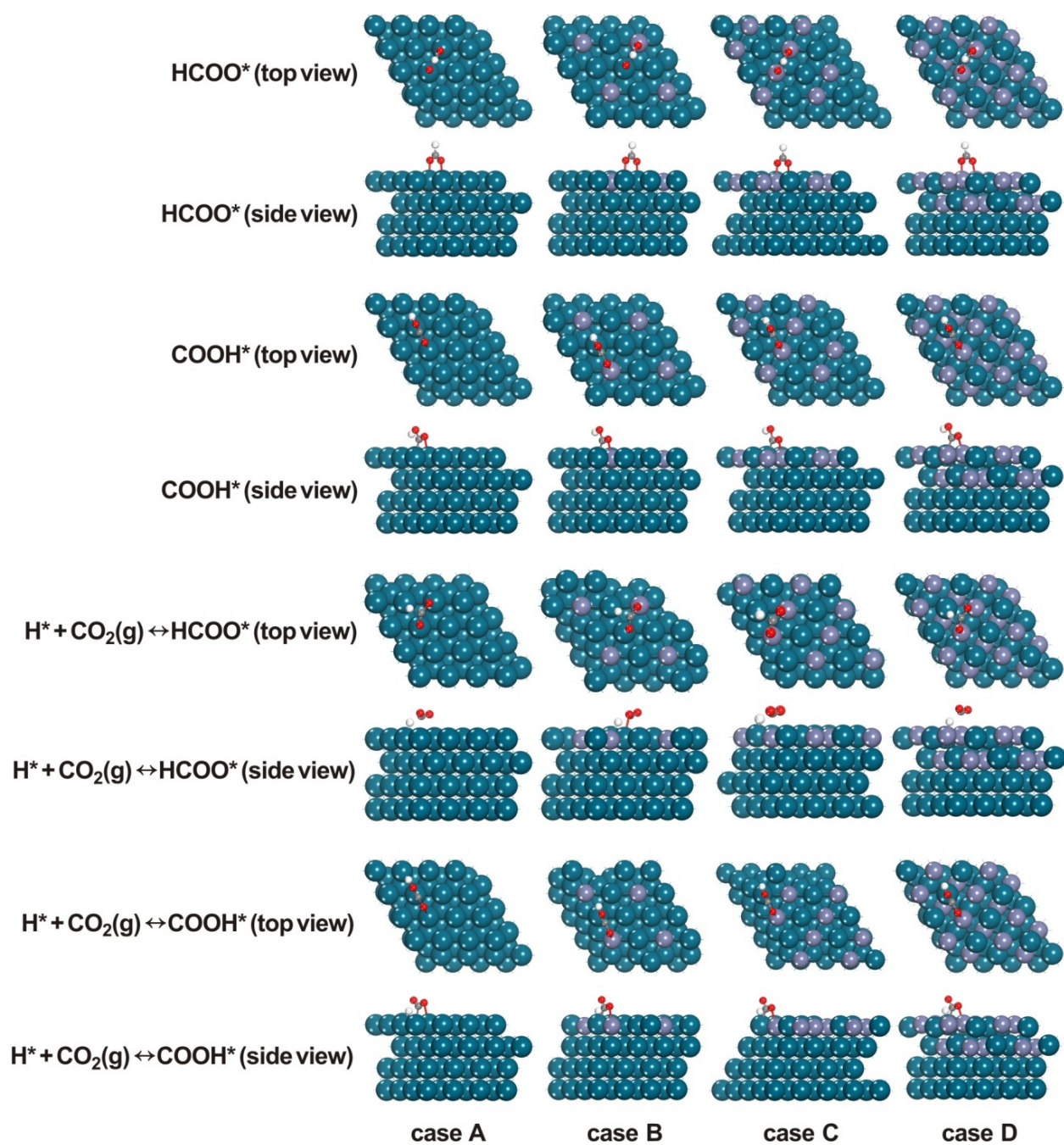


**Figure 7-20** Corresponding structures of the species in  $\text{CO}_2$  hydrogenation to  $\text{HCOO}^*$  and  $\text{COOH}^*$  at cases A-D.

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# Chapter 8 Conclusions and future work

## 8.1 Conclusions

In this thesis, it is presented the development of a new method for the rational preparation of supported bimetallic NPs with tunable compositions. Through the establishment of a type II hetero-junction in support, controllable amounts of metallic atoms can be derived from the reduction of the metal oxide support with the assistance of a supported noble metal. As a result, extremely small bimetallic NPs, namely PdFe, RhFe, PdCo, PdNi, and PdZn, with various noble metals to modifier atom ratios have been synthesized. From DFT modeling calculations, it is shown the *d*-band structure of the bimetallic NPs is associated with the type of the modifier atoms and the compositions of bimetallic NPs.

In the Pd system:

- (i) The *d*-band filling drops with the progressive incorporation of early transition metals due to their lower electron occupancy of *d* orbitals than Pd.
- (ii) With similar ratio of Pd: M, the *d*-band filling increases from PdFe to PdCo, PdNi and PdZn due to the increasing number of valence electrons in the transition metals ( $\text{Fe } 3d^6 < \text{Co } 3d^7 < \text{Ni } 3d^8 < \text{Zn } 3d^{10}$ ).
- (iii) The *d*-band center position of Pd-based bimetallic NPs rises with increasing concentration of the late first row transition metals if their energy of 3*d* orbital is higher than that of Pd 4*d*.

These novel bimetallic catalysts have been applied in the direct catalytic conversion of biomass or biomass derived molecules to value-added chemicals. It has been demonstrated that the catalytic performance is mainly governed by the electronic structure of the bimetallic NPs. For

the Pd system, the catalytic ability of Pd can be altered from selective C-C bond cleavage to selective C-O bond cleavage in the hydrogenolysis of vicinal diol unit of biomass. High *d*-band filling and *d*-band center position favour the C-O bond breaking, while the selective C-C bond rupture is achieved by the reduction of *d*-band filling. Through rational selection of the catalyst, specific small alcohol molecules (e.g. methanol, ethanol, propanol) can be produced with high selectivity from the catalytic conversion of biomass or biomass derived molecules. To simplify the catalytic system, ethylene glycol (EG) is mainly used as the starting material. EG is a derivative from biomass and is usually regarded as a model for biomass molecules with repeating vicinal diol units. Future investigation will focus on the applications of these bimetallic NPs in the conversion of real world biomass molecules, e.g. glycerol, glucose, etc.

PdZn bimetallic NPs with a core(Pd)-shell(Zn) structure have also been employed in methanol synthesis via CO<sub>2</sub> hydrogenation while CO<sub>2</sub>/H<sub>2</sub> can be produced from the low temperature reforming of biomass resource. The Zn shell not only enhances the activity and the selectivity of Pd metal towards methanol synthesis, but also suppresses the RWGS reaction in which CO is produced as a by-product. Methanol can be produced as the main product over CO on the Zn rich PdZn surface, even at low pressure. The methanol TOF reaches  $1.9 \times 10^{-1} \text{ s}^{-1}$  with a selectivity of 70% at 2 MPa. The excellent catalytic performance in CO<sub>2</sub> hydrogenation makes PdZn a promising catalyst for methanol synthesis from renewable resource under mild conditions. Although high methanol TOF has been achieved, the weight time methanol yield of the PdZn catalyst is not yet sufficient enough to justify the industrial scale application. The methanol weight time yield is mainly restricted by the blockage of Pd active site by the thick Zn decoration shell and the relatively large bimetallic particle size. Therefore, future research should focus on

the structure optimization of the PdZn bimetallic phase to maximize the exposure of Pd site while maintaining the Zn modulation, and eventually improving the methanol yield.

## 8.2 Future perspectives

Gradual depletion of non-renewable fossil fuel resources and growing environmental problems have caused significant concern. To relieve our dependence on non-renewable fossil fuels, the need for exploring renewable synthesis routes (e.g. from biomass) of our daily stock is ever pressing. As advocated by the noted chemist George Olah (Nobel chemistry laureate), renewable methanol can be used as both energy carrier and chemical synthesis intermediate to drive our society.[1,2] As a result, the strategic position and demand for methanol as both fuel and platform chemical are expected to rise. We believe that more research efforts will be devoted to the development of methanol synthesis from renewable resources in the foreseeable future.

Novel catalysts with high activity and selectivity toward target product are urgently needed in the development of renewable chemical synthesis routes. Alloying with secondary elements has been demonstrated as an effective method in enhancing the catalytic properties of monometallic NPs, particularly the active noble metal NPs. A facile method for the synthesis of small supported bimetallic catalysts with tunable chemical compositions has been developed, and the catalytic performances of the synthesized catalysts are presented in detailed in this thesis. However, the main challenge lies in the geometric blockage of noble metal surface by the modifier atoms. This greatly reduces the efficiency of precious metal resources. Simple methods for preparing new bimetallic clusters with favourable electronic modulation but high accessibility of noble metal surface will, therefore, receive growing interest. Moreover, new methods beyond alloying for

modulating the electronic structure of noble metal, without geometric alternation, are also highly desired from science and technology perspectives.

## References

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- [2]. G. A. Olah, A. Goeppert and G. K. S. Prakash, *Beyond oil and gas: the methanol economy*, Wiley-VCH; John Wiley, Weinheim; Chichester, **2006**.