Theoretical study on the reaction mechanism of DMFC and DFAFC facilitated by palladium-based catalysts

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**Theoretical Study on the Reaction Mechanism of
DMFC and DFAFC Facilitated by Palladium-based
Catalysts**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2011

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DFAFC Facilitated by Palladium-based Catalysts**

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Abstract

Electrocatalytic surface reaction has attracted more and more interests from both the experimental and the theoretical researchers. It is of great significance to have a deep insight of the mechanism of the reaction in the electrochemistry system. The mechanism of direct methanol fuel cell (DMFC) catalyzed by palladium electrode under both neutral and alkaline condition is theoretically studied. Under neutral condition, the energy barrier for the first dehydrogenation of CH_3OH via either C–H bond scission or O–H bond scission is very high which leads to the palladium shows very low activity towards methanol decomposition under neutral condition. However, under alkaline condition the reaction barrier of the O–H bond scission of CH_3OH is effectively reduced by the adsorbed OH and gives out the first intermediate, CH_3O . The further reaction via CH_2O and HCO to CO and then the CO combines with the adsorbed OH to COOH. And the COOH directly accounts for the final product of CO_2 . This reaction mechanism is in line with the reported experimental results.

The direct formic acid fuel cells (DFAFCs) are regarded as one of the most promising alternative to H_2 and alcohol based fuel cells and they have attracted great interest in the past decades. However, the reaction mechanism of DFAFCs with metal surface as the electrolytes is still unclear. Even the experimental results have given the controversial phenomena. We proposed three reaction mechanisms to analysis the experimental phenomena. Four possible adsorption geometries of the adsorbed formic acid are selected as the initial reactant. The hydrogen centered formic acid and the oxygen and hydrogen centered formic acid accounts for the direct pathway. The oxygen and hydrogen centered formic acid and the oxygen centered formic acid will lead to the

reaction pathway where the formate serves as an intermediate. And the oxygen and hydrogen centered formic acid, the oxygen centered formic acid and the bi-oxygen centered formic acid contributed to the formate which serves as the site blocking species.

Finally, to make the study more systematic, we have carried out the research of catalyst design. We aim to design the palladium based catalyst through the sublayer structure. By the examination of the electronic structure of the Pd(1 1 1) surface with sublayer structure, we have revealed that its Fermi-energy level, the *d*-band center and the work function can be adjusted by the verification of the sublayer structure. Based on Brønsted–Evans–Polanyi (BEP) relation, Sabatier principle, work function theory and the *d*-band theory, we propose the possibility of the new palladium based catalyst.

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List of Symbols and Abbreviations

DMFC- direct methanol fuel cell

DFAFC-direct formic acid fuel cell

UHV - ultra high vacuum

TPF - temperature programmed desorption

HREELS - high resolution electron energy loss spectroscopy

PM-IRAS -polarization-modulation infrared absorption spectroscopy

SSIMS - static secondary-ion mass spectrometry

PFDMS - pulsed field decomposition mass spectrometry

DFT - density functional theory

PEM - polymer electrolyte membrane

IRAS - infrared reflection-absorption spectroscopy

RHE - reversible hydrogen electrode

HF - Hartree Fock

FFT - fast fourier transform

PP – pseudopotentials

US-PP -Ultra-Soft pseudopotential

PAW - Projector Augmented Wave potential

NEB - nudged elastic band

VASP - Vienna Ab Initio Simulation Package

STM-scanning tunneling microscope

E_r - reaction energies

E_a - activation barriers

TS - transition state

ATR-SEIRAS -absorption spectroscopy in the attenuated total reflection mode

HOMO - highest occupied molecule orbital

LUMO - lowest unoccupied molecule orbital

BEP relation - Brønsted–Evans–Polanyi relation

fcc - face-centered cubic

hcp - hexagonal close-packed

Chapter 1. Research Background and Literature Review

1. 1 Research Background

Fuel cell, as the power generation systems, provides a clean alternative to the conventional systems that based on fossil fuel. Fuel cell systems have many advantages, such as high efficiency and use of easily available hydrocarbons. What's more, the by-product of fuel cell is water which makes it environmentally friendly. Fuel cell has been used extensively and successfully in spacecrafts, transportations, mobile phones and laptops. It is promising field of exploring the energy. Thus, more and more efforts are on to commercialize the fuel cell into application.^{1,2}

Fuel cell is an electrochemical device that converts the chemical energy of the fuel and reactant into electrical energy and heat. The conversion is continuously in condition that the reactants keep being supplied to the electrodes. It is very similar to a battery because they both operate on the electrochemical energy conversion but there is a significant difference; a fuel cell does not store fuel and reactant but a battery does. And a fuel cell operates on a continuous supply of fuel and reactant. This makes fuel cell kind of similar to a heat engines. However, fuel cell does not combust the fuel and give out gases (but an engine does). Fuel cell burns the fuel and reactant by the means of current and the product is water. Unlike the heat engine whose efficiency is limited by the Carnot efficiency, the fuel cell works on an electrochemical principle and thus it can give out a higher efficiency than a heat engine. So a fuel cell carries out the continuous energy conversion from chemical form to electrical form with high efficiency but hardly

pollution and making fuel cell an excellent choice for power generation¹.

A fuel cell is composed of a fuel electrode (anode) and an oxidant electrode (cathode) which is separated by an ion-conducting electrolyte as shown in Fig.1.1. The electrodes are externally connected by a load to complete the electronic-ionic circuit. Take the basic fuel cell with hydrogen as the fuel and oxygen as the oxidant as an example. The hydrogen is ionized at the fuel electrode (anode) to release hydrogen ions and electrons. The ion-conducting electrolyte allows only the ionic flow and resists the electronic flow. Thus, the electrons flow out through the electrical circuit and arrive at the oxidant electrode (cathode) after supplying power to the external load whereas the hydrogen ions flow through the ion-conducting electrolyte to reach the cathode. Oxygen at the cathode side interacts with the electrons and the hydrogen ions to produce the water. The overall reaction is the combination of the reactions of anode and the cathode.

Fig.1.1 Operation of a fuel cell

1.2 Simulation of fuel cell

To improve the performance of fuel cell and finally make the fuel cell commercially viable, tremendous effort is being poured both experimentally and theoretically. And with the development of the computing science, simulation of heterogeneously catalyzed reactions by *ab initio* quantum mechanical methods is playing an increasingly important in the understanding of existing catalysts (cathode and anode) and the rational design of new electrode. In principle, the application of theoretical modeling technical can provide synergistic guidance for experiments with the aim that elucidate the controlling heterogeneously catalyzed surface reaction. A typical heterogeneously catalyzed reaction involves, firstly, the adsorption of the reactants onto the catalyst surface, then the transformations of the reactants on the catalyst surface, and finally the desorption of the products from the catalyst surface. Theory has served as a powerful tool to analysis the adsorption (physical adsorption and chemisorption), transformation, diffusion and surface reactivity selectivity.

Simulation is powerful as the predictive method to estimate the adsorption energies, reaction energies (thermodynamics), activation barriers (kinetics), and vibrational frequencies for ultra high vacuum (UHV) and vapor-phase systems and the results agree well with experiment. However, the theoretical efforts is facing great challenge because of the complex of solution phases and the applied potentials. The great improvement in computational power and the increase of efficiently computation algorithms have largely improved the capacity of simulation the complex environments, such as the solution and surface potential. This theoretical manner then start to serve as an effective complement to experiments and it offers a more principle method to well-

understand the electrochemical and electrocatalytic process.

1.3 Objectives and scopes of this work

For the ultimate goal of the electrocatalytic research goes to the design of electrocatalysts which relies on the throughout understanding of the reaction mechanism that take place at the electrodes surface. Then it is of great significance to have a deep insight of the mechanism of the reaction in the electrochemistry system. Being served as the model of the interaction between the metal surface and the small molecules, the DMFC facilitated by the metal surface is a series of typical surface reaction. And within the entire metal surface, the Pd and Pd-based electrode are a part of the most promising replacement to the normally platinum ones. Platinum is one of the very first and most important electrodes that have been studied both experimentally and theoretically. However, the high price and limited supply of platinum constitute a major barrier to the development of platinum electrodes. Pt-free electrocatalysts such as palladium and palladium based electrocatalysts is one of the most promising candidates to replace the platinum and platinum-based ones. Moreover, the palladium shows good activity for the methanol, 1-propanol and 2-propanol oxidation in alkaline medium¹³ and the Pd-based electrocatalysts have been used for formic acid and hydrazine electro-oxidation in acid medium⁵¹⁻⁵³. Those interesting experimental phenomena attract us for a detailed investigation on the palladium electrode.

The reaction behavior is much better for the methanol decomposition on the Pd (1 1) surface under alkaline condition compared with that in the acid solution as well as the gas phase condition. It is therefore attracted us to have a systematic theoretical

investigation on the mechanism. And we proposed that the hydroxyl must play an important role in the reaction. We aim to study the reaction mechanism of methanol decomposition with palladium surface as the catalyst to analyze the experimental phenomena. As we have discussed, the simulation of the solution phase is of great importance but really computing time consuming. How to simulate the solution phase with affordable computing recourse is a challenge for all theoretical researchers. In this thesis, we used a simple but robust model to simulation the solution phase. It turns out that this model catches the significant point of the solution effect and supports the experimental phenomena very well.

As a following up, the mechanism of formic acid oxidation on Pd(1 1 1) surface is also studied to make the research work more systematic. The direct formic acid fuel cells (DFAFCs) have attracted great interest in the past decades for they are regard as a promising alternative to H₂ and alcohol based fuel cells. However, the mechanism of formic acid decomposition and oxidation on metal surface is still suspended. Even the experimental results have given the controversial phenomena. We proposed three reaction mechanisms to analysis the experimental phenomena.

Finlay, it comes to the real problem, the catalyst design issue. We aim to design the novel catalyst through the sublayer structure Pd(1 1 1) surface. By the examination of the electronic structure of the surface, we have found that the Fermi-energy level, the *d*-band center and the work function of the Pd(1 1 1) surface can be adjusted by the sublayer structure. Based on Brønsted–Evans–Polanyi (BEP) relation, Sabatier principle, work function theory and the d-band theory, we propose the probability of the new catalyst.

1.4 Literature review on the direct methanol fuel cell (DMFC)

Fuel cell has been accepted as a more clean and realistic alternative to traditional combustion engine for their superiority at increasing power densities, efficient, and lower cost.³ Fuel cells with alcohol as the fuel have attracted great attention during the past decades. Direct alcohol fuel cells (DAFCs) are promising fields because they exhibit much higher energy density than the traditional hydrogen and natural gas fuel.^{4,5} Methanol decomposition and oxidation on metal and metal-oxide surface are prototypical reactions of DAFCs. Because such reaction is a typical model of the surface reactions that take place between the noble metal-based surface and the alcohols and small organic molecules.⁶⁻⁸ And the platinum and platinum based surface serving as the electrode have been widely studied from both experimental and theoretical perspective. Unfortunately, the supply of the traditional platinum is limited which leads to its price are very high. And this disadvantage inhibits the development of platinum catalyzed fuel cell. To replace the platinum electrocatalysts, the palladium and palladium based ones are a significant part of the most prospective candidate.⁷⁻¹³

Methanol decomposition and oxidation reaction is one of the most investigated reactions in fuel cells due to its significance in the development of direct methanol fuel cells (DMFCs) technology. Experimentally, the adsorption of methanol onto various metal surfaces has been widely investigated.^{7,14-28} It is widely accepted that as a general phenomenon, the CH₃OH dissociatively adsorb (through O–H bond scission) on metal surfaces and give out the intermediates of methoxyl.²⁹ Furthermore, It is also pointed out that on the Group VIII metals, the decomposition of methanol often takes place at temperatures of about 200 K. Investigations by experimental instrument such as

temperature programmed desorption (TPD), isotopic labeling and high resolution electron energy loss spectroscopy (HREELS) have reported that methanol dissociative decomposition occurs via the O–H bond scission on Ru(0 0 1),²³ Ni(1 1 1),^{14,15} Ni(1 1 0),^{16,17} Rh(1 1 1),^{25,26} Pt(1 1 1),¹⁸ Pd(1 0 0),^{21,22} Fe(1 0 0),²⁴ and Rh(1 0 0) surface,²⁷ for stable methoxyl (CH₃O) intermediates have been detected. Study on polarization-modulation infrared absorption spectroscopy (PM-IRAS) has pointed out that the decomposition of CH₃OH to CO and H₂ on Pd(1 1 1) surface takes place via CH₃O, CH₂O, HCO to CO.³⁰ Static secondary-ion mass spectrometry (SSIMS) has been applied to study the methanol decomposition on Pd(1 1 1) surface and it has detected PdOCH₃⁺ species which supports the existence of the methoxyl species.³¹ The formaldehyde species has been detected around 170 K on Pd(1 1 1) surface by means of HREELS, which leads to adsorbed carbon monoxide and H atoms at around 300 K.³² HREELS experiments have also detected formyl on Pd(1 1 0) surface at 110 K during methanol decomposition.³³ By means of pulsed field decomposition mass spectrometry (PFDMS), HCO⁺ and CH₂O⁺ ions were detected during Pd(1 1 1) single crystal surface catalyzed methanol decomposition which give the evidence of the existence of CH₂O and HCO.³¹

Theoretical investigations revealed that the CH₃OH decomposition on transition metal surface is dominant by the C–H bond scission and O–H bond scission in both vacuum phase and aqueous phase. For experimental report has pointed out that in ultra-high vacuum, the C–O bond scission of methanol has hardly been detected.^{19,20,22,32,34} By means of density functional theory (DFT), theoretical study has pointed out that the C–O bond scission only take place at very slow-speed and it turns out to be a by-process of the dominant dehydrogenation (C–H bond scission and O–H bond scission) pathway.³⁵ Thus,

in current thesis we focus on the dominant dehydrogenation involved reaction pathways.

Fig.1.2 Cyclic voltamograms of methanol, 1-propanol and 2-propanol oxidation on palladium electrode in 1.0M KOH + 1.0M alcohol solution containing (sweep rate of 5mVs^{-1})¹³.

Although, many research works have been carried out, a detailed and systematic mechanisms study of Pd surface catalyzed methanol decomposition under neutral condition including all decomposition steps is still inadequate for completeness. Furthermore, the experiment has recently revealed that the palladium shows a much better catalytic performance to methanol decomposition and oxidation reaction under alkaline condition (as showed in Fig.1.2) than under neutral condition where the

palladium shows quit little or even no reactivity to methanol.¹³ Such a different experimental phenomena interest us for a systematic study on the mechanism of methanol decomposition on palladium surface under both neutral and alkaline condition. By means of DFT calculation, we will study all reaction steps involved under both neutral and alkaline condition. We will also investigate the variation of the activation barriers of each elementary reaction steps that involved. Wherever possible, the optimized geometries, reaction energies, activation barrier as well as the proposed reaction mechanism are compared with the available literature results.

1.5 Literature review on the direct formic acid fuel cell (DFAFC)

Formic acid (HCOOH) is served as the fuel for polymer electrolyte membrane (PEM) fuel cells because formic acid shows several superiorities such as high theoretical and experimental open cell potential, easy storage and transportation. Formic acid is week acid and in aqueous phase, it partially dissociates and leads to the formate anions which reduces fuel crossover through the polymer electrolyte membrane.³⁶ All these advantages make formic acid as a promising candidate for portable applications and it is proposed to be one of the most promising candidate as the potential power sources.^{37,38} The decomposition and oxidation mechanisms of the simplest organic fuel, such as methanol, formaldehyde and formic acid molecules, are quite different although they are similar in structure.³⁹⁻⁴¹ Thus, it is of great significance to have a fundamental insight on their decomposition and oxidation mechanism then it will give powerful advise on the efficient catalyst design.

The decomposition and oxidation of HCOOH on Pt-group metals electrodes has been a hot topic during the past decades for the reason that its relevance in low-temperature fuel cells and its status as a fundamental electrochemical oxidation reaction.⁴²⁻⁴⁵

Numerous experimental studies have presented different perspectives on what may be the relevant intermediates in formic acid oxidation. *In situ* infrared reflection-absorption spectroscopy (IRAS) experiments detected adsorbed carbon monoxide, a product of formic acid dehydration and also a poisonous species.^{46,47} Both Osawa *et al.*⁴⁸⁻⁵⁰ and Behm *et al.*⁵¹⁻⁵³ have pointed out that at potentials below 0.3 V, the polycrystalline surfaces is covered with adsorbed carbon monoxide (*vs* the reversible hydrogen electrode (RHE)), decreasing carbon monoxide is accompanied with increasing formate (HCOO) concentrations between 0.3 and 0.7 V (*vs* RHE). Then the surfaces are dominated by adsorbed formate above 0.9 V (*vs* RHE). Wilhelm *et al.* initially hold the opinion that either COH or CHO would be the reactive intermediate. However, others have long assumed it is carboxyl (COOH).^{44,54} Using the same IR techniques, Behm *et al.* indicated that formate is a site-blocking species and weakly adsorbed HCOOH could then be the intermediate.⁵¹⁻⁵³ They proposed that CO₂ is directly obtained via the dehydrogenation of a weakly adsorbed formic acid. Formic oxidation experiments at elevated temperatures lead to increased currents but decreased concentrations of formate, suggesting either that formate formation is slower than formate decomposition or that the formate pathway is not dominant.

In contrast, by the same IR spectroscopy, Osawa *et al.* have concluded that formate (HCOO) is the reactive intermediate whose oxidation to carbon dioxide is

regarded as the rate-determining step.⁴⁸⁻⁵⁰ The oxidation current density of HCOOH against potential curve is very similar to the band intensity (potential dependence) of the adsorbed formate. Samjeske *et al.*⁵¹⁻⁵³ have proposed the formate-involving pathway for HCOOH decomposition and oxidation on Pd surface. They have featured the adsorbed formate as an active intermediate to CO₂. Macia *et al.* who performed HCOOH electrooxidation with Pt(1 1 1) as the electrodes at a low Bi coverage and draw a similar conclusion.⁵⁵

Theoretically, first-principles calculations are expected to help clarify these conflicting experimental phenomena. Unfortunately, quite few theoretical reports available on the reaction mechanism of formic acid electrocatalytic decomposition or its electrocatalytic oxidation. Notably, computational results obtained by Neurock *et al.* have showed that adsorbed carboxyl might be the reactive intermediate while formate is a spectator which supports the experiments by Behm *et al.*⁵⁶ Neurock *et al.* have also concluded that an applied potential has very little effect on the activation barriers of the adsorbed formate, but applied potentials influence the oxidation of carbon monoxide significantly.⁵⁶ Wang and Liu have used continuum solvation approaches to model the Pt/H₂O interface and they have suggested that a weakly adsorbed HCOOH with its C–H bond pointing to the surface is the reactive intermediate and the applied potentials have minor effects on formic acid oxidation barriers.⁵⁷ Lim *et al.* have systematically investigated the adsorption of formic acid and the possible intermediates involved on Pt(1 0 0), Au(1 0 0) and Pt@Au (Pt decorate Au surface) surface.⁵⁸ Their calculated thermodynamic results support the experimental phenomena that compared with the pure palladium surface, the formic acid oxidation may be facilitated by the Pt@Au surface.⁵⁸

Apart from the puzzles on the mechanism, it is also still an unclear question that whether formate is an intermediate or it is a site blocking species. It is of great necessary to study the formic acid decomposition and then give suggestions on the catalyst design issue.

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Chapter 2. Theories and Calculation Methods

2.1 General background

2.1.1 Density functional theory (DFT)

Density functional theory (DFT) has been developed from last century and become popular for compare with other methods, it is less computationally intensive with same accuracy. In Hartree Fock (HF) approximation, it is fundamental to search the wavefunction and hence obtain all information on the system. However, the N -electron wavefunction is very complicated as it depends on $4*N$ variables. And the wavefunction based calculations lead to an unmanageable size and a huge computational consume. Nevertheless, instead of the wavefunction, DFT provides solutions by the introduction the electron density $\rho(\mathbf{r})$.

The modern DFT originates from the well-known Hohenberg-Kohn theorems (Hohenberg and Kohn, 1964).¹ At the beginning, the DFT stating that the ground state electronic energy E_0 is a function of ground state electron density ρ_0 and can is depicted by $E_0 = E_0[\rho_0]$. And the ground state density formally determines the all electronic properties of all states. Then the DFT is further refined as ground state only theory. Because the function is carrying the ground state energy of the system, if and only if the real ground state density ρ_0 is imported to the input density, it delivers the lowest energy

Although Hohenberg-Kohn theorems have established the theoretical basis of DFT, Kohn and Sham improved it into a more practical application of this theory. They

proposed a method which is structurally similar with the HF method and provided an avenue for the implementation of DFT.²

2.1.2 Plane waves

For an extended and even infinite system, the calculations of the one-electron wavefunction are formidable. One solution is assuming that the system could be represented by periodic cell of atoms which is periodically repeated in all dimensions. The periodic lattice with lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ produces a periodic potential and imposes the uniform periodicity on the density. Therefore, for such systems, instead of using basic expansion of spin orbitals $\{\chi_i\}$, plane waves are used for the expansion of orbitals as the wavefunction are a complete and orthogonal set of function. The plane wave is defined as

$$f_G^{\text{PW}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \exp[i\mathbf{G} \cdot \mathbf{r}] \quad (2.1.)$$

where the Ω is the volume of the box and is calculated as the determinant of $\mathbf{h} = [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3]$

$$\Omega = \det \mathbf{h} \quad (2.2.)$$

and $\mathbf{G}$ is the reciprocal space vectors

$$\mathbf{G} = 2\pi(\mathbf{h}^t)^{-1} \mathbf{g} \quad (2.3.)$$

where $\mathbf{g} = [i, j, k]$ is the triple of integer value.

Based on Bloch's theorem, a periodic function can be expanded as

$$\psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{L}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} \psi(\mathbf{G}) \exp[i\mathbf{G} \cdot \mathbf{r}] \quad (2.4.)$$

where $\psi(\mathbf{r})$ and $\psi(\mathbf{G})$ are related by three-dimensional Fourier transform. The direct lattice vectors $\mathbf{L}$ connects equivalent points in different cells.

Then the Kohn-Sham orbitals of a periodic system is defined in the plane wave basis

$$\Phi(\mathbf{r}) = \Phi_i(\mathbf{r}, \mathbf{k}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} c_i(\mathbf{G}, \mathbf{k}) \exp[i(\mathbf{G} + \mathbf{k}) \cdot \mathbf{r}] \quad (2.5.)$$

where $\mathbf{k}$ is a vector in the first Brillouin zone and $c_i(\mathbf{G}, \mathbf{k})$ are complex numbers.

In the practical calculations, the infinite sums over $\mathbf{G}$ vectors and cells have to be truncated. And the integral over the Brillouin zone has to be approximated by a finite sum over special $\mathbf{k}$ -points. Generally, for a highly disorder system in the periodic supercell with large lattice constants, the Brillouin zone integration is efficiently calculated by a single point at $\mathbf{k} = 0$, the so-called Γ -point.

Kohn-Sham potential converges rapidly with the increasing modulus of $\mathbf{G}$ determines the truncation of the plane wave basis. So, the coefficients $c_i(\mathbf{G}, \mathbf{k})$ of the plane waves with relatively lower kinetic energy are more significant than those with relatively higher kinetic energy. Only vectors $\mathbf{G}$ with kinetic energy no higher than a maximum cutoff E_{cutoff}

$$\frac{1}{2} |\mathbf{G}|^2 \leq E_{\text{cutoff}} \quad (2.6.)$$

are included in the basis (Γ -point integration is assumed). With choice of plan wave basis, only maximum cutoff E_{cutoff} controls the precision of the calculation within the approximations of DFT, instead of the type and number of functions in calculation based on basis set.

Plan wave basis possess several advantages. First, it does not depend on the position of nuclei so there is no Pulay force³ but Pulay force exists when using Gaussian basis functions. Secondly, the derivatives in real-space are simply multiplication in $\mathbf{G}$ -space. It makes the operators and energy expression easily calculated. Finally, the connection between real-space and $\mathbf{G}$ -space are efficiently connected by Fast Fourier Transform (FFT).

2.1.3 Pseudopotentials (PP)

In typical chemical reactions, normally the inner core electrons are essentially inert and only the valence electrons are involved in the calculation. Therefore, with the aim to minimize the plane wave basis, it is reasonable to omit of the core electrons which are represented together with the nuclei. And angular momentum dependent pseudopotentials is introduced to describe all electrostatic and quantum-mechanical interactions of the valence electrons with the cores (such as Pauli repulsion and correlation and exchange between core and valence electrons, the nuclear Coulomb attraction screened by the core electrons).⁴⁻⁷ Outside the core region, these PP reproduce the true potential and valence orbitals and inside, these PP still much weaker and smoother. Therefore, The PP approximation is to remove the core electrons and replace the true nuclear potential $V_{\text{ion}}(\mathbf{r})$ created by the core electrons and the nuclei with a weaker pseudopotentials $V_{\text{ion}}^{\text{PP}}(\mathbf{r})$. With the removal of core electrons, the wavefunctions ψ are described by pseudo wavefunctions $\psi_{\text{ion}}^{\text{PP}}$. $\psi_{\text{ion}}^{\text{PP}}$ is expected to be smooth and nodeless close to the nuclear core region which ensure that plane wave basis with small energy cutoff E_{cutoff} can represented wavefunctions effectively.

Fig.2.1 The schematic demonstration of the full all electronic wavefunction. The electronic potential varies with the effect of the distance r_c from the atomic nucleus is presented with solid lines. And the corresponding pseudo potential and wavefunction is plotted with dashed lines.

Fig.2.1 shows the schematic demonstration of the full all electronic wavefunction. The electronic potential varies with the effect of the distance r_c from the atomic nucleus is presented with solid lines. And the corresponding pseudo potential and wavefunction is plotted with dashed lines. It is noticed that the all electron and pseudo electron values are identical outside a given radius r_c . Because of the strong ionic potential within the core electron occupied region, the wavefunction ψ rapidly oscillates in order to maintain orthogonality with the core electrons. The expansion of ψ in the plane wave basis

requires a large cutoff energy E_{cutoff} . The pseudopotential is composed such that the pseudo wavefunction $\psi_{\text{ion}}^{\text{PP}}$ is smooth and nodeless. So, a relatively small E_{cutoff} is required. Beyond the ionic core radius r_c , $\psi_{\text{ion}}^{\text{PP}}$ and PP must perform exactly the same as the wavefunction ψ and the true ionic-potential.

There are two terms to evaluate the performance of pseudopotential: softness and transferability. A softer pseudopotential means that the one with larger r_c which enables the use of smaller E_{cutoff} . And transferability ensures that identical pseudopotential is applicable in various chemical environments with desirable computational accuracy. However, it has been confirmed that the pseudopotential with fine transferability demands r_c around the outermost maximum of ψ and $\psi_{\text{ion}}^{\text{PP}}$ must demonstrate the same norm as the ψ within r_c as the norm-conservation pseudopotential. So that $\psi_{\text{ion}}^{\text{PP}}$ reproduces ψ beyond r_c . And therefore, softness and transferability of pseudopotential have to compromise each other.

Vanderbilt's Ultra-Soft pseudopotential (US-PP)^{7,8} and Projector Augmented Wave potential (PAW)^{9,10} are commonly used pseudopotentials. US-PP has been proposed by Vanderbilt in the early 1990s. For calculations of the same accuracy, it attains not only much softer (smoother) pseudo wavefunctions but also uses quit fewer plane waves. The pseudo wavefunctions with the core region are soft enough and it is possible for a drastic reduction in the cutoff kinetic energy. The US-PP calculations are extensive used to describe the physical and chemical properties of complex ionic systems consisting of. The PAW potential has been introduced by Blöchl in 1994.⁹ The basic idea of PAW is to divide the wavefunction into three parts, atomic-like partial waves $\{\phi_i\}$, auxiliary partial

waves $\{\tilde{\phi}_i\}$ expanded within atomic sphere regions and auxiliary wavefunction $\{\tilde{\psi}_i\}$ expanded outside the spheres (as shown in Fig.2.2).

$$|\psi\rangle = |\tilde{\psi}\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle p_i | \tilde{\psi} \rangle \quad (2.7.)$$

Fig.2.2 Wavefunction decomposition of PAW method

The minimization of energy is gotten by variation of the auxiliary wavefunction which is computationally demanding less. Unlike US-PP approaches, PAW method avoids the introduction of pseudopotential for the core electrons. And the core electrons are decomposed with the same way as the valence electrons without the projector operators and are constant during calculation. Thus, PAW method is an all-electron method and works with frozen-core approximation directly.

2.1.4 Periodic boundary condition (PBC)

Periodic boundary condition is imposed by the plane wave basis set to the simulation of large system. It is used for calculations on extended periodic systems (such

as crystals, bulk) and amorphous condensed phases (such as amorphous solids and liquids). With the aim to simulate a gaseous molecular system, a vacuum region around the molecular system should be taken into consideration by using a supercell with large lattice parameter $\mathbf{L}$. With the size of the supercell increases, the total energy changes with respect to $\mathbf{L}$ and converges until the distances between the molecular system and the periodic images are large enough so that they have negligible interaction. In general, the inter-image distance required to imitate gas phase conditions is around 6 Å.

2.1.5 Nudged Elastic Band (NEB)

The NEB is a saddle points finding method that works by constrained optimization of a number of intermediate images with known reactant and product.¹¹⁻¹⁵ The constrained optimization is fulfilled by implementing spring forces along the band between images and by projecting out the component of the force due to the potential perpendicular to the band. During constrained optimization, each image optimizes to the lowest energy and at the same time the image maintains equal space with their neighboring images. There are some improvements to the NEB method and among which the climbing-image NEB (cNEB) is the most commonly used one.

Fig.2.3 Comparison of the NEB (blue dots) and cNEB (red dots). The selected model is an adsorbed Al atom on the Al(1 0 0) surface. This is a diffusion process caused by an exchanging process between the adsorbed atom with the atom from the substrate atom.

As a modification of NEB, the cNEB drives up the highest energy image to the saddle point (transition state). The highest energy image receives the true force along the tangent is inverted but does not the spring forces along the band. With cNEB, the image tries to minimize its energy in all the other directions but maximize energy along the band. When it come to a convergence, the highest image will be right at the exact saddle point (transition state). For the highest image has moved to the transition state and the

spring force does impose on it, the space to the images on both side of the highest image will be different

Fig.2.3 shows the comparison of the NEB (blue dots) and cNEB (red dots). The selected model is an adsorbed Al atom on the Al(1 0 0) surface. This is a diffusion process caused by an exchanging process between the adsorbed atom with the atom from the substrate. It could be noticed how the cNEB has driven up the image with highest energy to the right transition state position.

2.2 Computational details in current thesis

For chapter 3, chapter 4 and chapter 5, the computations are carried out with the Vienna Ab initio Simulation Package (VASP).¹⁶⁻¹⁸ By using the plane-wave basis set, Kohn-Sham equations are solved self-consistently. To make the plane-wave basis set finite, the cutoff dynamic energy of 200 eV is used. At this cutoff energy (200 eV), calculations have been carried out to verify the convergence of the computed electronic energies. Ultra-soft scalar relativistic pseudopotentials (US-PP) are imposed to reproduce the nuclei and core electrons.⁸ All electronic structure calculations are completed with the Perdew Wang 91 GGA exchange correlation functional.¹⁹ The interaction at the Brillouin zone is described with $7 \times 7 \times 1$ Monkhorst-Pack²⁰ grid with a generalized Gaussian smearing technique.²¹ The cell used is a three-layer slabs which is periodically repeated in a 3×3 super cell and the surface coverage is 1/9 (monolayer). The vacuum region is set as 13 Å between any two cells. The coordinate of bottom two layers atoms are frozen. However, the top layer and the adsorbate atoms are free to optimize. cNEB method with

eight images linear interpolated between the optimized reactants and products states is imposed to investigate the reaction mechanisms.

We are using a cut off energy of 200 eV based on the following 2 reasons: Firstly, the present cut off energy ensures reliable adsorption properties. Adsorption is serving as the first and the most important steps in the surface reactions, the present cutoff dynamic energy ensure a very good description of the adsorption properties that the binding energies as well as the optimized geometries are in good accordance with the literature (refer to chapter 3 for details). Secondly, more importantly, we focus on the relative Pd catalytic ability under neutral and alkaline media. With present cutoff dynamic energy value, we can clearly observe the difference of the reaction barriers. The experimental phenomena that the palladium is more active to methanol under alkaline condition than that under neutral condition are effectively explained by theoretical simulations. Under alkaline condition, the adsorbed hydroxyl facilitates the reaction by lowering the O-H bond scission barrier of methanol from 121 kJ/mol to 77 kJ/mol. Then the product namely the adsorbed methoxy could further decompose to the final product. And the rather high reaction barriers of both C-H (133 kJ/mol) and O-H bond scission (121 kJ/mol) leads to the Pd shows very low reactivity to methanol under neutral condition (refer to chapter 3 for details).

For chapter 5, cutoff kinetic energy of 450 eV was used to investigate the electronic properties of the surface. Here much higher cutoff kinetic energy has been introduced than that used for the search of the reaction mechanism in chapter 3 and 4. The selection of the cutoff kinetic energy is depends on the purpose of the research. For the investigation of the mechanism, we aim to depict the reaction potential surface and to

trace the trend but not the very accurate numbers. Based on the study of the adsorption energy and the optimized geometries which show good accordance with the literature, it concluded that the parameters we used are reasonable to give out reliable results. However, for the calculation of the surface electronic properties, much higher cutoff kinetic energy is needed to depict the subtle characterization of the surface. We have done the benchmark test before the research and it showed that the 450 eV cutoff kinetic energy is the optimized value which could make the plane wave basis finite and give out accurate results and at the same time it ensures the computational consuming is affordable. Ultra-soft scalar relativistic pseudopotentials are imposed to reproduce the nuclei and core electrons.⁷ All electronic structure calculations are performed with the PW91 GGA²² exchange correlation functional.

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Chapter 3. Effective Reaction Mechanism of DMFC on Pd(1 1 1) Surface Facilitated under Alkaline Condition

3.1 Introduction

3.1.1 Background

It is commonly accepted that there are three steps in the surface reaction. Firstly, the reactants get close to the surface and until adsorbed on to it. Secondly, the reactants interact with the surface further to accomplish the reconstruction to the products. Finally, the products process a desorption procedure and leave far away from the surface. Here the adsorption serves as initial and also one of the most significant processes for the surface catalytical reaction. And the exact nature of the adsorption (the interaction between the surface and the adsorbate) depends on the details of the species involved. Usually, the adsorption is generally classified as physisorption and chemisorption based on the interaction intensity.¹

The interaction between the adsorbate and the surface has essential importance with the reaction barrier which is directly affect the reaction rate. Volcano curve (also known as the Sabatier's principle) is commonly accepted as a fundamental principle in heterogeneous catalysis field.² It states that an effective catalyst will bind the reactants strongly but not so strongly that no products can desorb. The experiments have revealed that a volcano-shaped curve will showed up if you draw the relationship of the activity of a specific reaction to a functional parameter of the catalyst surface. These volcano-shaped

relations are interesting for they guide the design of novel effective catalysts. As long as the adsorption is crucial for the surface reaction, we will discuss in some detail for adsorption of all the involved adsorbate which is relative to the methanol decomposition on Pd(1 1 1) surface from both energetic and structural aspect.

3.1.2 Models in current thesis

In this thesis, we simulate the alkaline condition with the adsorbed hydroxyl. We support this method based on the following reasons.

Firstly, the existence of the adsorbed hydroxyls on Pd surface under alkaline condition is commonly accepted. For example, it has been pointed out that under alkaline condition at lower potentials, the adsorption of OH⁻ ions follows the Temkin-type isotherm on palladium electrode. And at higher potentials, its Tafel slope increased.³

Secondly, the quantity of the adsorbed OH under alkaline condition is much larger than that under neutral condition. It has been reported that the increase of alkaline concentration leads to a higher coverage of the adsorbed hydroxyl. Under stronger alkaline condition, the adsorption of OHs is dominant on the palladium electrode.³ Indeed, one has OH on the surface under neutral condition but the amount of the adsorbed OH would be much lower than that under alkaline condition. The chance of adsorbed OH to interact with the surface intermediate would be negligible. But the alkaline medium provides the needed quantity of the adsorbed OH which will participate in the surface reaction.

Thirdly, simulating the alkaline condition by means of the adsorbed hydroxyl is widely used in the works based on density functional theory (DFT). Here are some

typical references. According to the DFT calculations, it is found that during the ethanol decomposition on Pd(1 0 0) surface the under alkaline condition, adsorbed hydroxyl species assists in lowering the reaction barrier of the CH₂CHOH species oxidizing to the acetic acid species.⁴ And the DFT calculations has also shows that under acidic condition, the continued decompositions of ethanol are hard because the hydroxyl species is rare. Conversely, both ethanol and sufficient hydroxyl can absorb on palladium surface under alkaline condition, leading to continuous ethanol electrooxidation.⁵

Finally, our main aim is to simulate the surface reaction. Surface is crucial for the surface catalyzed reactions because the surface could facilitate the reaction by enhance the reactivity and selectivity

Based on the above discussion, it is reasonable to use the adsorbed hydroxyl in this work to simulate the effects of alkaline condition.

3.2 The optimized geometry of all the possible adsorbate

The calculation on the adsorption of the adsorbate involved in the methanol decomposition on Pd(1 1 1) surface have been performed. And the possible adsorption geometries at various adsorption sites are carefully examined aiming to obtain the most stable equilibrium geometries.

The binding energy is used to describe the strength of the adsorption and it is defined as the energy released during the adsorption (as showed in equation 1)

$$E_b = E_{ad} + E_{slab} - E_{ad/slab} \quad \text{Eq.(1)}$$

Where $E_{ad/slab}$ is the optimized total energy of the adsorbed adsorbate and the surface.

E_{ad} is the optimized energy of the adsorbate in the gas phase and E_{slab} is the optimized

energy of the clean Pd(1 1 1) surface. From this definition, a strong adsorption will release more energy which will reflect at a more positive binding energy. So a higher binding energy implies a more favorable interaction between the adsorbate and the surface.

Geometrically, there are three typical adsorption site for the Pd(1 1 1) surface, the top, bridge site. If the adsorbate is interacting with an atom of the very first layer, we define the adsorption site as the top site. If the adsorbate is interacting with two surface atom, we named the adsorption site as bridge site. While, if the adsorbate is placed at a center of three surface atoms (Fig.3.1), the adsorption site is defined as hollow site. According to the geometry, if the adsorbate is vertically facing an atom from the second layer, it is a *fcc* (face-centered cubic) hollow site, and if it is facing an atom from the third layer, it a *hcp* (hexagonal close-packed) hollow site.

Fig.3.1 Top view of the adsorption site for the Pd(1 1 1) surface. The number 1, 2 and 3 are corresponding to the top first, top second and the third layer.

Fig.3.1 shows top view of the adsorption site for the Pd(1 1 1) surface. The number 1,

2 and 3 are corresponding to the top first, top second and the third layer. The atoms labeled as “1” denoted a top adsorption site and the atoms labeled as “2” and “3” denoted the hollow site. As long as the adsorption is important to understand the reaction mechanism, all the possible adsorption sites are examined for each adsorbate to find out the most stable adsorption geometry.

3.2.1 Methanol (CH_3OH)

It is confirmed both experimentally and theoretically that the interaction between the methanol and the metal surface occur via donation and acceptance of lone pair electrons.⁶⁻⁹

Fig.3.2 The optimized binding energy and the adsorption configurations (in angstrom) of methanol when it binds to Pd(1 1 1) surface via various adsorption site. The binding energy (in kJ/mol) is shown in the parentheses. With the aim of clarity, the bottom two layers are not shown.

Fig.3.2 shows the optimized geometry while the methanol adsorbs onto the Pd(1 1 1) surface via different adsorption sites. The binding energy (in kJ/mol) is shown in the parentheses for each adsorption configuration, respectively.

Methanol molecule is close shell, so the integration is characterized as van der Waals' forces. And it is proved by the binding energies results that calculated by DFT. The binding energies are attached with Fig.3.2 and they are relatively small indicating the weak interaction between the methanol and the Pd(1 1 1) surface. And the most stable adsorption geometry is occurred by top site adsorption where methanol molecule interacts with the atop site Pd(1 1 1) surface through the oxygen center. The Pd–O bond is rather long as 2.34 Å (Fig.3.2) which agrees well with the reported data of 2.24 ~ 2.46 Å.^{7,10} The binding energy is calculated to be 31 kJ/mol which agree well with the literature results of 23 ~ 34 kJ/mol.^{7,10,11}

3.2.2 Methoxy (CH_3O)

On Pd(1 1 1) and Pd(1 0 0) surface, by means of experimental technique, stable methoxy intermediates are detected.¹²⁻¹⁴ The adsorption of methoxy which appears to take place via the interaction between the oxygen atom and the surface is well confirmed.

It is reports that the methoxy shows the most favorite to the three-centered hollow sites when it is adsorbed on Pd(1 1 1) surface by both slab model and cluster model calculations.^{10,11,15} Fig.3.3 shows the optimized binding energy and the adsorption structure (in angstrom) of methoxy when it adsorbed onto Pd(1 1 1) surface via various adsorption site. The binding energy (in kJ/mol) is shown in the parentheses. The methoxy presents relatively weak adsorption at the top site while it shows the strongest adsorption at the hollow site. Based on our calculation, the CH_3O prefers to bind Pd(1 1 1) surface through its O atom with no special preference between *hcp* and *fcc* sites. From Fig.3.3, it is noted that the methoxyl demonstrate the largest binding energy when it adsorbed at *hcp*

site. The length of the Pd–O bond, 2.11 Å, is in agreement with literature (2.16 and 2.24 Å).^{10,15} The binding energy is 177 and 193 kJ/mol for *fcc* and *hcp* site which is in accordance with the literature.^{10,11,15}

Fig.3.3 The optimized binding energy and the adsorption configurations (in angstrom) of methoxy when it binds to Pd(1 1 1) surface via various adsorption site. The binding energy (in kJ/mol) is shown in the parentheses. With the aim of clarity, the bottom two layers are not shown.

3.2.3 Hydroxymethyl (CH_2OH)

The methanol decomposition initially through the C–H bond scission and leads to the CH_2OH is the main reaction pathway for methanol decomposition on the Pt (1 1 1) surface. Thus, CH_2OH is selected to be a possible intermediate in our calculation.

The electron is rich around the carbon atom of hydroxymethyl radical, it makes the hydroxymethyl incline to interact with the metal surface via the carbon atom center. This is confirmed by our DFT results that the optimized structure of adsorbed hydroxymethyl shows that the interaction takes place between a top Pd atom and the carbon atom. The results are summarized in Fig.3.4.

Fig.3.4 The optimized binding energy and the adsorption configurations (in angstrom) of hydroxymethyl when it binds to Pd(1 1 1) surface via various adsorption site. The binding energy (in kJ/mol) is shown in the parentheses. With the aim of clarity, the bottom two layers are not shown.

Based on the binding energy results, the hydroxymethyl shows the strongest interaction with the Pd(1 1 1) surface while it adsorbs at the top site with the Pd–C bond as long as 2.06 Å, agreeing well the 2.10 Å from the literature.¹¹ The CH₂OH adsorbs onto the Pd(1 1 1) surface strongly and demonstrate a binding energy of 179 kJ/mol which agrees well with 177 kJ/mol of literature.¹¹

3.2.4 Formaldehyde (CH₂O)

The formaldehyde molecule shows a relatively weak adsorption on the Pd(1 1 1) surface via a parallel configuration.

Fig.3.5 The optimized binding energy and the adsorption configurations (in angstrom) of formaldehyde when it binds to Pd(1 1 1) surface via various adsorption site. The binding energy (in kJ/mol) is shown in the parentheses. With the aim of clarity, the bottom two layers are not shown.

And we have examined all the possible adsorption configurations which are summarized in Fig.3.5. The CH_2O prefer the top-bridge-top configuration most where the π bond of the $\text{C}=\text{O}$ shows the best interaction with the Pd(1 1 1) surface. With most stable top-bridge-top configuration, the $\text{C}=\text{O}$ group features almost parallel to the Pd(1 1 1) surface which leading to a similar bond length of the Pd-C and Pd-O bonds (2.22 and 2.16 Å). As reported by the literature, this top-bridge-top adsorption model is established as the most preferred configuration on clean Pt-group metals surface.⁷ The binding energy is 39 kJ/mol for the most stable configuration which is in accordance with the 43 ~ 54 kJ/mol in the literature.^{10,11,16}

3.2.5 Formyl (HCO)

Based on our DFT results, the formyl radical prefer to binds to the Pd(1 1 1) surface via its carbon atom as showed in Fig.3.6.

Fig.3.6 The optimized binding energy and the adsorption configurations (in angstrom) of formyl when it adsorbs onto the Pd(1 1 1) surface via various adsorption site. The binding energy (in kJ/mol) is shown in the parentheses. With the aim of clarity, the bottom two layers are not shown.

The largest value of the binding energy is obtained with the formyl adsorbs to the surface via the *hcp* adsorption site. However, the Pd–C bond is 2.10, 2.11 and 2.63 Å respectively at the *hcp* adsorption site. The Pd–C bond varies and indicates that the adsorption site is not a strictly *hcp* site any more. A same phenomenon is found for the *fcc* adsorption site. On Pd(1 1 1) surface, the formyl shows similar preference through different adsorption site because the energy difference of the binding energy is within 15 kJ/mol when it binds to different adsorption sites. So we choose the top site as the optimized stable configuration where its binding energy is 205 kJ/mol. The result agrees with the literature results of 214 ~ 237 kJ/mol.^{10,11,16}

3.2.6 Carbon monoxide (CO)

Many studies on CO adsorption over lots of metal surfaces have been performed. And it is reported that carbon monoxide binds strongly to the surface and is hard to take part in the further reaction which make CO a the typical poison of the electrode.¹⁷ It is

established that adsorption of CO on metal surfaces occur via the donation of electron from carbon monoxide molecule (the 5σ orbital) to the metal and then a back-donation from the metal surface into the carbon monoxide ($2\sigma^*$ orbital).¹⁸ Fig.3.7 shows the optimized adsorption configuration of CO on the Pd(1 1 1) via different adsorption site.

Fig.3.7 The optimized binding energy and the adsorption configurations (in angstrom) of carbon monoxide when it binds to Pd(1 1 1) surface via various adsorption site. The binding energy (in kJ/mol) is shown in the parentheses. With the aim of clarity, the bottom two layers are not shown.

Based on our DFT results, the carbon monoxide prefers to binds to the Pd(1 1 1) surface via the hollow site with no distinct preference between the *fcc* and *hcp* site. This is supported by the experiment that scanning tunneling microscopy indicates that CO on Pd(1 1 1) occupies hollow sites.¹⁹ The binding energy is 172 and 173 kJ/mol for the *fcc* and *hcp* site adsorption respectively which is in line with the reference data of 178 kJ/mol.¹⁵

3.2.7 Hydroxyl (OH)

By means of electron energy loss (EEL) experiments, it is reported that the

hydroxyl prefer to bind to Pd(1 0 0) surface through the O atom.²⁰

Fig.3.8 The optimized binding energy and the adsorption configurations (in angstrom) of hydroxyl when it binds to Pd(1 1 1) surface via various adsorption site. The binding energy (in kJ/mol) is shown in the parentheses. With the aim of clarity, the bottom two layers are not shown.

Base on this experimental phenomenon, we examined four possible adsorption configurations which are summarized in Fig.3.8. Base on our DFT results, the hydroxyl shows much more strong binding at the two-fold bridge and 3-fold hollow site than the top site. The largest binding energy, 231 kJ/mol, is obtained at the *hcp* site with the Pd–C bond about 2.20 Å. This is in good accordance with of 214 kJ/mol and 2.14 Å in the literature.²¹

3.2.8 Carboxyl (COOH)

CO₂ is detected as the final product during the methanol decomposition under alkaline condition. One of the possible reaction pathways is that the carbon dioxide is the produced by the decomposition of the carboxyl.²²⁻²⁴ Thus, the carboxyl is selected as one of the possible intermediates.

Fig.3.9 The optimized binding energy and the adsorption configurations (in angstrom) of carboxyl when it binds to Pd(1 1 1) surface via various adsorption site. The binding energy (in kJ/mol) is shown in the parentheses. With the aim of clarity, the bottom two layers are not shown.

The electrons are rich around carbon atom which makes the carboxyl prefer to bind to the Pd(1 1 1) surface via its carbon atom. Being a radical, the carboxyl adsorbs strongly on the surface with no particular preference between different adsorption site (the difference is within 15 kJ/mol). The optimized hollow site adsorption incline to collapses to the bridge or top site adsorption for the Pd–C bond length varies a lot. The largest adsorption energy, 207 kJ/mol, is obtained at the top site adsorption which is selected as the most stable configuration. At the atop site of Pd(1 1 1) surface, the carboxyl interact with the Pd(1 1 1) surface via the Pd–O bond as long as 1.99 Å which agrees well with the literature results, 1.94 Å.²² The binding energy is 207 kJ/mol. Relevant results are summarized in Fig.3.9.

3.2.9 Water (H_2O)

For the methanol decomposition is alkaline media, the water is the other final product besides carbon dioxide. Thus water is one of the candidates that we have studied

its adsorption.

Fig.3.10 The optimized binding energy and the adsorption configurations (in angstrom) of water when it binds to Pd(1 1 1) surface via various adsorption site. The binding energy (in kJ/mol) is shown in the parentheses. With the aim of clarity, the bottom two layers are not shown.

Electrons are rich around its O atom so the interaction should be via the donation of the electrons from the oxygen atom to the surface. Scanning tunneling microscope (STM) experiments point out that water molecule prefers to interact with the Pd(1 1 1) surface at a top site via the O atom.²⁵ Based on this experimental results, we examined the adsorption of water on Pd(1 1 1) surface thoroughly (Fig.3.10).

The adsorption of water with the Pd(1 1 1) surface occur by the donation of the long pair electrons of the oxygen to the surface. Based on the binding energies, the interaction is a weak adsorption and the largest adsorption energy is obtained at the top site. The binding energy at the most favorable (top) site, 17 kJ/mol, is agree well with the literature result, from 21 to 32 kJ/mol.^{21,26,27}

3.2.10 Conclusion

Fig.3.11 The optimized binding energies and adsorption configurations (in angstrom) of all the adsorbate involved in the methanol decomposition on the Pd(1 1 1) surface. The binding energy (in kJ/mol) is shown in the parentheses. With the aim of clarity, the bottom two layers are not shown.

The optimized binding energies and adsorption configurations (in angstrom) of all the adsorbate involved in the methanol decomposition on the Pd(1 1 1) surface are summarized in Fig.3.11. The binding energy (in kJ/mol) is shown in the parentheses. With the aim of clarity, the bottom two layers are not shown. Table 3.1 shows the optimized adsorption geometry, binding energy (in kJ/mol) and the adsorption configurations (in angstrom) of various adsorbates compared with the literature. It is

noticed that our results shows a good accordance with the literature which indicating that the methods and all the parameters used in our calculation is accurate enough to give out reliable results.

Table 3.1 The optimized adsorption geometry, binding energy (in kJ/mol) and the adsorption configurations (in angstrom) of various adsorbate compared with the literature.

adsorbent	adsorption geometry		binding energy		adsorption configuration	
	results	literature	results	literature	results	literature
CH ₃ OH	top	top	31	23~34	2.34	2.25~2.46
CH ₃ O	<i>fcc</i> or <i>hcp</i>	<i>fcc</i> or <i>hcp</i>	193	185	2.11	2.16~2.24
CH ₂ OH	top	Top	179	177	2.06	2.10
CH ₂ O	parallel	parallel	39	43~54	2.22; 2.16	2.12; 2.09
CHO	top	top	205	214~237	1.95	2.00
CO	<i>fcc</i> or <i>hcp</i>	<i>fcc</i> or <i>hcp</i>	173	178	2.10	2.04
OH	<i>fcc</i> or <i>hcp</i>	<i>fcc</i> or <i>hcp</i>	231	214	2.20	2.14
COOH	top	top	207	\	1.99	1.94
H ₂ O	top	top	17	21~31	2.32	2.10

3.3 The reaction mechanism of CH₃OH decomposition on Pd(1 1 1) surface

To have a better understanding on how palladium electrode catalyzes the methanol decomposition reaction, detail studies on the reaction mechanisms including both thermodynamic and kinetic study are explored. With the optimized adsorption structure of all the possible intermediates (Fig.3.11) that involved in CH₃OH decomposition on palladium electrode, we have studied the detailed reaction mechanism which will be discussed in details in this chapter. To get the complete reaction pathways, we have analyzed every possible reaction step that involved.

3.3.1 Methanol decomposition under neutral condition

The CH₃OH gets close to the surface and then adsorbed onto the surface. For the first step, it could initially decompose via either the C–H bond scission (C–H bond scission pathway) giving out CH₂OH and H or the O–H bond scission (O–H bond scission pathway) leading to CH₃O and H. Here the C–H bond scission pathway and O–H bond scission pathway is named by the specific first dehydrogenation step. For C–H/ O–H bond scission pathway, the first dehydrogenation of methanol is through the C–H / O–H bond scission and the following dehydrogenation would through either C–H bond scission or O–H bond scission. The reaction energy (E_r) and the reaction barrier (E_a) for each reaction step involved in DMFC facilitated by Pd(1 1 1) surface are summarized in Table 3.2. Reaction mechanism of the DMFC with Pd(1 1 1) surface as the electrode under neutral condition through C–H as well as O–H bond scission pathways are attached as Figure 3.12 and Figure 3.13, respectively.

Fig.3.12 The reaction mechanism of CH_3OH decomposition on $\text{Pd}(1\ 1\ 1)$ surface under neutral condition begin with the C–H bond scission. Numbers with and without parentheses are the reaction energies and activation energies (in kJ/mol), respectively. And the corresponding geometry of reactants, transition states as well as products is also attached. The products of the adsorbed H and the surface are omitted.

C–H bond scission pathway (start with C–H bond scission). The reaction mechanism of $\text{Pd}(1\ 1\ 1)$ surface catalyzed methanol decomposition under neutral condition begin with C–H bond scission is summarized in Figure.3.12.

$\text{CH}_3\text{OH} = \text{CH}_2\text{OH} + \text{H}$: It has been showed that the methanol prefer to adsorbs on $\text{Pd}(1\ 1\ 1)$ surface through the oxygen center (Fig.3.11). The methyl group tilts toward the $\text{Pd}(1\ 1\ 1)$ surface and with the participation of a surface palladium atom the C–H bond is activated. With the activation, the O atom relocated step by step when carbonic

hydrogen getting close to the Pd(1 1 1) surface. At the transition state, the palladium surface interacts with both carbon and hydrogen atom and forming Pd–H bond as long as 1.97 Å and Pd–C bond as long as 2.44 Å. And the C–H bond is weakened and elongated to 1.53 Å of the transition state (Fig.3.11) from 1.08 Å of the adsorbed CH₃OH. The C–H bond breaking of methanol on Pd(1 1 1) surface is endothermic by 27 kJ/mol and the reaction barrier is 133 kJ/mol.

$CH_2OH = CH_2O + H$: As the product of the C–H bond scission of methanol, the adsorbed CH₂OH could further decompose by its O–H or the C–H bond scission. Based on our calculation, the activation of its O–H bond presents a lower reactivation barrier than its C–H bond scission which makes the O–H bond scission more favorable. When the hydroxyl hydrogen is attracted by the palladium surface, this O–H bond is activated. The C–O group is optimized by a rotation until it gradually finds its most stable position. At the transition state, the bond is elongated to 1.16 Å. The activation of O–H bond results in the formation of Pd–O bond (2.16 Å,) and Pd–C bond (2.22 Å, Fig.3.11). The O–H bond break of hydroxymethyl is endothermic by 15 kJ/mol with it demonstrating an activation barrier of 68 kJ/mol (Fig.3.11).

Fig.3.12 shows the reaction mechanism of CH₃OH decomposition on Pd(1 1 1) surface under neutral condition initially started with the C–H bond activation. Because the O–H bond scission pathway and C–H bond scission pathway share the same component that CH₂O decomposes to CO via HCO. Thus, it will be discussed in details in O–H bond scission pathway section.

Fig.3.13 The reaction mechanism of methanol decomposition on Pd(1 1 1) surface under neutral condition begin with the O–H bond scission. Numbers with and without parentheses are the reaction energies and activation energies (in kJ/mol), respectively. And the corresponding geometry of reactants, transition states as well as products is also attached. The products of the adsorbed H and the surface are omitted.

O–H bond scission pathway (start with O–H bond scission). Fig.3.13 shows the reaction mechanism of methanol decomposition on Pd(1 1 1) surface under neutral condition begin with the O–H bond scission.

$CH_3OH = CH_3O + H$: Besides the C–H bond scission, methanol may possible to decompose via the O–H bond scission. Methanol is activated when the hydrogen atom of the OH group is getting close to the surface until a surface palladium inserts. While the H moves close to the surface, the O–H bond is elongated to 1.74 Å from 0.96 Å (adsorbed

CH₃OH) and at the transition state the distance between the O and the surface Pd is 2.23 Å. The C–O bond slightly shrinks to 1.51 Å of the CH₃O from 1.53 Å of CH₃OH. The hydrogen atom of the OH adjusts to the surface until a *hcp* hollow position while the O–H bond is activated. According to our computational results, the O–H bond scission of methanol exhibits a reaction barrier of 121 kJ/mol with the reaction energy of 46 kJ/mol which agrees well with the literature result of 45 kJ/mol.¹¹ During methanol oxidation and decomposition on Pd(1 1 1) surface, the methoxyl is detected by PM-IRAS spectra (around 2900 cm⁻¹)²⁸ and the existence of methoxy species is supported by the observation of PdOCH₃⁺ species by means of SSIMS.²⁹

$CH_3O = CH_2O + H$: The methoxy further decomposes to the formaldehyde via C–H bond scission. The C–H bond is activated as one of the hydrogen atom is abstracted by the Pd(1 1 1) surface which leads to the carbonyl group gradually tilts toward the surface until a top-bridge-top structure. At the transition state, the C–H bond is elongated to 1.33 Å. The C–O bond length changes very little (1.42 Å at the transition state, and 1.37 Å at the gas phase methoxy) which reveals that the TS is more reactant-like rather than product-like. This reaction step presents a reaction barrier of 92 kJ/mol and the reaction energy is 15 kJ/mol. The formaldehyde is identified by PM-IRAS with the phenomena that the adsorbed CH₂O developed with time (peak at 1305 and 1255 cm⁻¹) which supports that it is intermediate species relative to the methanol decomposition on Pd(1 1 1) surface.²⁸ The observation of the CH₂O⁺ ions by PFDMS technique also proves the existence of CH₂O.²⁹ HREELS spectrum for layerly adsorbed CH₃OH indicates the participation of CH₂O in CH₃OH decomposition reaction ($\pi_{CO} = 705$ cm⁻¹, $\nu_{CO} = 1420$ cm⁻¹).³⁰

$CH_2O = HCO + H$: For the decomposition of CH_2O , together with its C–H bond scission, the carboxyl group rotates until it is almost perpendicular to the Pd(1 1 1) surface. The C–H bond is elongated to 2.04 Å at the transition state from 1.10 Å (the adsorbed CH_2O). And the C–O bond at the transition state is 1.20 Å which is similar to the theoretical value (1.17 Å in gas-phase formyl) which makes the transition state structure more product-like. This reaction step encounters a barrier of 54 kJ/mol and give out reaction energy of 36 kJ/mol. By means of PFDMS, the HCO^+ ions is detected which support the existence of HCO.²⁹ It is also reported that adsorbed HCO species (peak at $\sim 1200\text{ cm}^{-1}$) developed with time suggesting that HCO is intermediate relevant to methanol decomposition on Pd(1 1 1).²⁸

$HCO = CO + H$: The last dehydrogenation leads to the CO. The C–H bond of formyl is activated by the bond length elongation which is accompanied with the rotation of the carboxyl group. The C–H bond is elongated to 1.16 Å at the transition state from the 1.10 Å of the initially adsorbed HCO. The C–H bond length is quite similar between the adsorbed HCO and the transition state which reveals the transition state is more reactant-like. The C–H bond scission of formyl is exothermic by 135 kJ/mol and demonstrates an activation barrier of 48 kJ/mol. During the Pd(1 1 1) surface catalyzed methanol decomposition and oxidation, by means of PM-IRAS the adsorbed carbon monoxide is observed (ν_{CO} at 1840 cm^{-1}) at millibar pressure.²⁸ Also the observation of the $PdCO^+$ ions by SSIMS supporting the presence with the CO.²⁹

Table 3.2 The reaction energy and activation energy (in kJ/mol) for all the possible reaction steps that involved in the methanol decomposition on Pd(1 1 1) surface without the existence of the adsorbed hydroxyl

	reaction energy	activation energy
$\text{CH}_3\text{OH} = \text{CH}_3\text{O}+\text{H}$	46	121
$\text{CH}_3\text{OH} = \text{CH}_2\text{OH}+\text{H}$	27	133
$\text{CH}_2\text{OH} = \text{CH}_2\text{O}+\text{H}$	15	68
$\text{CH}_3\text{O} = \text{CH}_2\text{O}+\text{H}$	-15	88
$\text{CH}_2\text{O} = \text{HCO}+\text{H}$	-36	54
$\text{HCO} = \text{CO}+\text{H}$	-135	48
$\text{COOH} = \text{CO}_2+\text{H}$	-43	74

The reaction mechanism of the Pd(1 1 1) surface catalyzed DMFC under neutral condition initially start with both C–H and O–H bond scission are summarized in Figure 3.12 and Figure. 3.13, respectively. On Pd(1 1 1) surface, the first dehydrogenation of methanol encounters with pretty high reaction barriers (133 and 121 kJ/mol for C–H and O–H bond scission, respectively) and these two reaction steps are both endothermic (27 and 46 kJ/mol for C–H bond scission and O–H bond scission, respectively). All these results in neither the hydroxymethyl nor the methoxyl are favored. The methanol is incline to desorb but not decompose. These computational results agree well with the experimental phenomenon which is reported that the palladium is barely active to

methanol under the neutral condition. Such high reaction barriers block the decomposition of methanol at the initial stage. Moreover, recent experiment demonstrate that the palladium is more active to methanol under alkaline condition.³¹

Table 3.3. The reaction energies for each possible steps during the methanol decomposition with and without the existence of the adsorbed hydroxyl (in kJ/mol)

Without OH catalyzed		With OH catalyzed	
Reaction Step	E_r	Reaction Step	E_r
$\text{CH}_3\text{OH} = \text{CH}_3\text{O} + \text{H}$	46	$\text{CH}_3\text{OH} + \text{OH} = \text{CH}_3\text{O} + \text{H}_2\text{O}$	23
$\text{CH}_3\text{O} = \text{CH}_2\text{O} + \text{H}$	-15	$\text{CH}_3\text{O} + \text{OH} = \text{CH}_2\text{O} + \text{H}_2\text{O}$	-96
$\text{CH}_2\text{O} = \text{CHO} + \text{H}$	-36	$\text{CH}_2\text{O} + \text{OH} = \text{CHO} + \text{H}_2\text{O}$	-86
$\text{CHO} = \text{CO} + \text{H}$	-135	$\text{CHO} + \text{OH} = \text{CO} + \text{H}_2\text{O}$	-175
$\text{CH}_3\text{OH} = \text{CH}_2\text{OH} + \text{H}$	27	$\text{CH}_3\text{OH} + \text{OH} = \text{CH}_2\text{OH} + \text{H}_2\text{O}$	-25
$\text{CH}_2\text{OH} = \text{CH}_2\text{O} + \text{H}$	15	$\text{CH}_2\text{OH} + \text{OH} = \text{CH}_2\text{O} + \text{H}_2\text{O}$	-33
$\text{CH}_2\text{OH} = \text{CHOH} + \text{H}$	47	$\text{CH}_2\text{OH} + \text{OH} = \text{CHOH} + \text{H}_2\text{O}$	-16
$\text{CHOH} = \text{CHO} + \text{H}$	-47	$\text{CHOH} + \text{OH} = \text{CHO} + \text{H}_2\text{O}$	-72

In the following section, we explore a theoretical study on the mechanism of methanol decomposition on Pd(1 1 1) surface under alkaline condition aiming to reveal a better understanding of such experimental phenomena.

3.3.2 Methanol decomposition under alkaline condition

Our experiment has recently revealed that palladium became more active to methanol under alkaline condition. Theoretical investigations on the reaction mechanism of methanol decomposition on Pd(1 1 1) surface facilitated by the adsorbed hydroxyl are essential to providing fundamental understanding on the catalytic mechanism.

Table 3.4 The reaction energy and the reaction barrier (in kJ/mol) for each the possible reaction steps that involved in methanol decomposition on Pd(1 1 1) surface with the existence of the adsorbed hydroxyl.

	reaction energy	activation energy
$\text{CH}_3\text{OH} + \text{OH} = \text{CH}_3\text{O} + \text{H}_2\text{O}$	23	77
$\text{CH}_3\text{OH} + \text{OH} = \text{CH}_2\text{OH} + \text{H}_2\text{O}$	-25	172
$\text{CH}_2\text{OH} + \text{OH} = \text{CH}_2\text{O} + \text{H}_2\text{O}$	-33	16
$\text{CH}_3\text{O} + \text{OH} = \text{CH}_2\text{O} + \text{H}_2\text{O}$	-96	77
$\text{CH}_2\text{O} + \text{OH} = \text{HCO} + \text{H}_2\text{O}$	-86	83
$\text{HCO} + \text{OH} = \text{CO} + \text{H}_2\text{O}$	-175	54
$\text{COOH} + \text{OH} = \text{CO}_2 + \text{H}_2\text{O}$	-105	68

Table 3.3 compares the reaction energy for each reaction steps between different environments. Under alkaline condition, the adsorbed hydroxyl serves as a strong driving force to make each reaction step more thermodynamic favorable. To well understand the reaction mechanism, a detailed study with the reaction barrier is required. The results are

summarized in Table 3.4. According to the results, the reaction pathways initially started with both C–H bond scission and O–H bond scission are summarized in Fig.3.14 and Fig.3.15, respectively.

C–H bond scission pathway (start with C–H bond scission). The reaction mechanism of Pd(1 1 1) surface catalyzed methanol decomposition under alkaline condition via C–H bond scission pathway is presented in Fig.3.14.

$CH_3OH + OH = CH_2OH: + H_2O$: At beginning, the dissociate hydroxyl ions and the dissociate methanol may interact with each other and then co-adsorb onto the Pd(1 1 1) electrode surface. For the optimized co-adsorption configuration, the oxygen atom of the adsorbed OH attracts the methylic hydrogen atom of the adsorbed CH_3OH to form a hydrogen bond there. At the transition state, the C–H bond is elongated to 1.74 Å the hydrogen bond from 1.08 Å of the co-adsorption complex. And the distance of hydroxyl O atom and the abstracted H atom is shrunk to 1.02 Å from 1.46 Å. With the existence of the adsorbed OH, the reaction step of C–H bond scission of methanol under alkaline condition presents a reaction barrier of 172 kJ/mol and this reaction step is exothermic by 25 kJ/mol (Fig.3.14). Draw a comparison with the same reaction step under neutral condition, the adsorbed OH does not enhance the activity ($E_a = 133$ kJ/mol under neutral condition and $E_a = 172$ kJ/mol under alkaline condition) from the kinetic perspective.

Fig.3.14 The reaction mechanism of methanol decomposition on Pd(1 1 1) surface under alkaline condition begin with the C–H bond scission. Numbers with and without parentheses are the reaction energies and activation energies (in kJ/mol), respectively. And the corresponding geometry of reactants, transition states as well as products is also attached. The products of the adsorbed H and the surface are omitted.

From the thermodynamic perspective, this reaction step is improved to more thermodynamic favorable (from endothermic by 27 kJ/mol and exothermic by 25 kJ/mol under neutral and alkaline condition, respectively) with the assistance of the adsorbed OH. To sum up, the existence of the adsorbed OH under alkaline condition makes the C–H bond scission of CH_3OH more thermodynamic favorable but less kinetic favorable. Regarding to C–H bond scission of CH_3OH , the existence of the adsorbed OH under alkaline condition has barely improve the activity of Pd(1 1 1) surface.

$CH_2OH + OH = CH_2O + H_2O$: As the product of the C–H bond scission of CH_3OH , the CH_2OH would further decompose through either its O–H bond scission or C–H bond scission. According to the computational results, its O–H bond scission is much more favored than its C–H bond scission under alkaline condition. When its hydroxyl H atom is attracted by the neighborly adsorbed OH, the O–H bond is activated by a bond length elongation. At the transition state, the O–H bond of CH_2OH is elongated to 1.35 Å from 0.97 Å and the hydrogen bond between the adsorbed hydroxyl O atom and the abstracted H atom is shrunk to 1.15 Å from 2.11 Å. Under alkaline condition, the O–H bond scission of CH_2OH is exothermic by 1 kJ/mol and demonstrates a reaction barrier of 16 kJ/mol with the existence of the adsorbed OH. Thus, the adsorbed OH under alkaline condition facilitates this O–H bond scission of CH_2OH both kinetically and thermodynamically.

Fig.3.14 shows the reaction mechanism of Pd(1 1 1) surface catalyzed methanol decomposition under alkaline condition through C–H bond scission pathway. The decomposition of CH_2O via CHO to carbon monoxide which then combines with the adsorbed OH to COOH and eventually decomposes to CO_2 is also a composition of the O–H bond scission reaction mechanism. Thus, it will be discussed in details in “O–H bond scission” section.

O–H bond scission pathway (start with O–H bond scission). The reaction mechanism of methanol decomposition on Pd(1 1 1) surface under alkaline condition initially started with O–H bond scission pathway is presented in Fig.3.15.

Fig.3.15 The reaction mechanism of methanol decomposition on Pd(1 1 1) surface under alkaline condition begin with the C–H bond scission. Numbers with and without parentheses are the reaction energies and activation energies (in kJ/mol), respectively. And the corresponding geometry of reactants, transition states as well as products is also attached. The products of the adsorbed H and the surface are omitted.

$CH_3OH + OH = CH_3O + H_2O$: The dissociated methanol and hydroxyl under alkaline condition interact and co-adsorb on the surface. On the surface, the H atom of the hydroxyl group (methanol) is attracted by the O atom of the adsorbed OH and form a hydrogen bond there. With the assistance of this hydrogen bond, the O–H bond is activated. At the transition state, the O–H bond is elongated from 0.97 Å to 1.48 Å and the hydrogen bond is shrunk from 1.87 Å to 1.12 Å. With the existence of the adsorbed OH, the reaction step of O–H bond break of CH_3OH is endothermic by 23 kJ/mol and

demonstrates an activation barrier of 77 kJ/mol (Fig.3.15).

Compare with the O–H bond scission of methanol under neutral condition, the surface OH effectively reduces the reaction barrier from 121 kJ/mol (under neutral condition) to 77 kJ/mol (under alkaline condition). From the kinetic perspective, it suggests the O–H bond scission under alkaline condition is more favorable. From thermodynamic perspective, the adsorbed OH drives the reaction energy from endothermic by 46 kJ/mol (under neutral condition) to endothermic by 23 kJ/mol (under alkaline condition) and makes this step more thermodynamic favorable. In conclusion, the adsorbed OH on Pd(1 1 1) surface is facilitating the O–H bond scission of methanol under alkaline condition both kinetically and thermodynamically. Comparing to the other possible reaction pathways, the O–H bond scission with assistance of the adsorbed hydroxyl is the most favorable pathway.

According to calculation, the CH₃O and CH₂O prefer to decompose directly rather than with the existence of adsorbed OH. The detailed discussion could be referred to section 4.1.2.

$HCO + OH = CO + H_2O$: Strongly adsorbed HCO then decomposes to the CO through C–H bond scission with the existence of the adsorbed OH. The C–H bond of the HCO is elongated to 1.23 Å to achieve the transition state where the distance of the abstracted H atom and the O atom of the adsorbed OH is 1.47 Å. This reaction step is exothermic by 175 kJ/mol and demonstrates a reaction barrier of 54 kJ/mol with the existence of the adsorbed OH. Compare to the same reaction step under neutral condition ($E_r = 135$ kJ/mol, $E_a = 48$ kJ/mol), the adsorbed OH does not promote the reaction from the kinetic perspective, but the adsorbed OH thermodynamically gives a strong driving

force. In conclusion, under alkaline condition the C–H bond scission of HCO might prefer with the existence of the neighborly adsorbed OH (Fig.3.14 and Fig.3.15).

$CO + OH = COOH$: Aiming to gain the final product, carbon dioxide which has been experimentally detected, one of the most popular reaction pathways is the combination of the adsorbed CO with the neighboring adsorbed OH which leads to the adsorbed COOH. The COOH is strongly adsorbed on to the surface and it further decomposes via the O–H bond scission leading to the CO₂.²²⁻²⁴ The CO and the OH firstly co-adsorbed on the surface and then the OH which is attracted by the neighborly adsorbed CO gets close to the adsorbed CO. The transition state is obtained when the C atom is 2.33 Å away from the hydroxyl O atom. The overall reaction energy for the combination of the adsorbed OH and CO is calculated to be endothermic by 50 kJ/mol with a reaction barrier of 96 kJ/mol (Fig.3.14 and Fig.3.15).

$COOH + OH = CO_2 + H_2O$: The chemisorption-adsorbed COOH decomposes via the O–H bond scission with the existence of the neighborly adsorbed OH. When its H atom is attracted by the neighborly adsorbed OH, the carboxyl's O–H bond is activated. The O–H bond is elongated to 1.12 Å to achieve the transition state where the abstracted H atom is 1.45 Å away from the O atom of the hydroxyl. The O–H bond scission of the adsorbed COOH with the assistance of neighborly adsorbed OH is exothermic by 105 kJ/mol with a reaction barrier of 68 kJ/mol (Fig.3.14 and Fig.3.15). By gas chromatography and PM-IARAS spectra, the CO₂ is observed as the product of CH₃OH decomposition and oxidation on Pd(1 1 1) surface.²⁸

3.4 Discussion and conclusion

So far, we have discussed every possible reaction steps involved in CH_3OH decomposition on $\text{Pd}(1\ 1\ 1)$ surface under both neutral and alkaline condition. Based on the different medium (neutral and alkaline) and the different first dehydrogenation step (C–H and O–H bond scission), we have studied 4 possible reaction pathways which are summarized in Fig.3.12, Fig.3.13, Fig.3.14, Fig.3.15, respectively. Among all these reaction pathways, the O–H bond scission pathway under alkaline condition (Fig.3.15) is the most energetically favorable one.

Under alkaline condition, the CH_3OH prefers to decomposes firstly via O–H bond scission to CH_3O and then by stepwise dehydrogenation via C–H bond scission to CH_2O , HCO and CO . Then the adsorbed join in the reaction by a the combines with CO to the COOH which occurs the last hydrogen distraction to the CO_2 . This reaction pathway is agrees well with the spectroscopical results of experiments. One of the highlights is with the assistance of the adsorbed OH , the final product is CO_2 .

For the most favorable reaction mechanism (Fig.3.15), the “ $\text{CH}_3\text{O} = \text{CH}_2\text{O} + \text{H}$ ” ($E_a = 92\text{ kJ/mol}$) and “ $\text{CO} + \text{OH} = \text{COOH}$ ” ($E_a = 96\text{ kJ/mol}$) exhibits the highest activation barrier. These phenomena are due to the structure and energy reasons. Structurally, the geometry from the perpendicularly adsorbed CH_3O to the parallely adsorbed CH_2O varies much which leads to more energy is need for the structure rotation. From the energytic perspective, the reactan CH_3O binding strongly to the surface ($E_b = 193\text{ kJ/mol}$), so it requires much energy to overcome the strong chemisorption. However, the product of CH_2O ($E_b = 39\text{ kJ/mol}$) binding weekly on to the surface which results in that less energy is released. These two factors accounts for the fact that C–H bond

scission of the CH_3O exhibits rather high reaction barrier. Similarly, the combination of the adsorbed CO and OH possesses high reaction barrier because both of them adsorb strongly ($E_b = 173$ and 231 kJ/mol, respectively) to the surface and lots energy is required to overcome such a strong dsorption.

The exploration of the reaction mechanism is important to catalyst poisoning issue. For the DMFC facilitated by the Pd(1 1 1) surface, both the HCO ($E_b = 206$ kJ/mol) and the CO ($E_b = 173$ kJ/mol) adsorb strongly onto the surface. However, the the HCO is ready to decompose for it excibits low reaction barrier ($E_a = 48$ kJ/mol under neutral condition and $E_a = 54$ kJ/mol under alkaline condition). While the further reaction of CO is blocked by the the high activation barrier and it leads to the CO less favorable to react nor desorb. This could explain why most electrochemica experiments revealed CO as the dominant poison species rather than the HCO.

The exploration of the reaction mechanism is important to the catalyst design. We suggest that the effect catalysit would excibit low reaction barrier to the C–H bond scission of CH_3O and the combination of the adsorbed CO and OH. It is interesting to notice that except for the first step, the reaction mechanism showed in Fig.3.14 (the C–H bond scission pathway under alkaline condition) possesses a more moderate reaction barrier. If we could refine the palladium catalysit which could effectively reduce the reaction barrier of the C–H bond scission of CH_3OH , the activity of palladium to CH_3OH under alkaline condition would be improved.

The dehydrogenation in solution may have some effect on the reaction however we believe the most import reaction steps that matters the catalysis performance are taken place on the surface. In fact, the dehydrogenation of methanol in solution supports the O–

H bond scission pathways, too. Methanol has a pK_a of *ca.* 15.5, in acid or neutral condition, the amount of the CH_3O^- by the dissociation in solution would be negligible (In a solution pH of 7, 1.0 mol/L methanol will give out the CH_3O^- with a concentration of *ca.* 0.003 $\mu\text{mol/L}$). Under alkaline condition, a higher amount of the methanol will dissociate to CH_3O^- ions (in a solution pH of 14, 1.0 mol/L methanol will give out the CH_3O^- with a concentration of *ca.* 0.03 mol/L). The amount CH_3O^- ions cannot be neglected. However, the dissociation effect is not strong enough as compared to the catalytical performance of the electrode. The adsorbed OH which has reduced the O–H bond scission from 121 kJ/mol to 77 kJ/mol plays the dominant role at improving the catalytical performance of Pd to methanol. Considering that the adsorbed OH is abundant under alkaline condition, we believe that the adsorbed OH on surface assisting the O–H bond scission of CH_3OH by decreasing the reaction barrier is the dominant force that facilitates the decomposition of methanol herein account for the better activity of Pd to methanol under alkaline condition.

In conclusion, Methanol decomposition pathway on Pd(1 1 1) surface under both neutral and alkaline condition involves every possible reaction step has been theoretically studied. Under neutral condition, the low activity of Pd towards CH_3OH under neutral condition is due to the very high activation barriers of the first step of methanol decomposition via both C–H bond and O–H bond scission. Under alkaline condition, the activity of palladium is improved because the activation barrier of the O–H bond scission is effectively reduced (from 121 kJ/mol under neutral condition to 77 kJ/mol under alkaline condition) with the assistance of the adsorbed OH on the surface. The CH_3OH first decompose to CH_3O which decomposes by stepwise dehydrogenation to form CH_2O ,

HCO and CO. The CO combines with the neighborly adsorbed OH to give out the COOH which directly accounts for the final product of CO₂.

3.5 References

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Chapter 4. Mechanistic Study for DFAFC with Palladium as the Electrode

4.1 Introduction

Being one of the most promising energy generator to alternate the H_2 and alcohol based fuel cells, direct formic acid fuel cells (DFAFCs) has attracted great interest in the past decades.¹⁻³ However, the reaction mechanism of formic acid decomposition and oxidation facilities by various metal surface is still unclear.

It is widely accepted that the electrochemical oxidation of $HCOOH$ on platinum surface takes place via a so called dual-path mechanism. Behm *et al.* have proposed that the formic acid oxidation mechanism should be considered as at least three different pathways, each starting from adsorbed formic acid (Scheme.1).⁴⁻⁶ The *indirect pathway* operates via a CO intermediate, which is a product of dehydrogenation of formic acid. The *direct pathway* likely operates via a weakly bound $HCOOH$ intermediate and is initiated by C–H bond scission. The *formate pathway* operates via a $HCOO$ intermediate and is initiated by O–H bond scission.

Scheme.1 Mechanistic scheme for electrochemical formic acid oxidation and decomposition

However, there are debates on whether the formate is an intermediate or it is the site blocking species.

Chen *et al.* claim that the weakly adsorbed formic acid molecule ($\text{HCOOH}_{\text{ads}}$) through the direct oxidation carries the most oxidation current while the adsorbed formate (HCOO_{ads}) is not an intermediate but a site-blocking species.^{4,5} And this point has been supported by the studies by Neurock *et al.* who theoretically investigate the palladium catalyzed formic acid oxidation via two possible routes, either adsorbed formate or carbonyl (COOH_{ads}).⁷ From first-principles calculations results, they have pointed out that in the main reaction pathway the adsorbed carbonyl plays the role of the intermediate and adsorbed formate serving as a site-blocking species.⁷

On the other hand, by means of surface-enhanced infrared absorption spectroscopy in the attenuated total reflection mode (ATR-SEIRAS), Osawa *et al.* has experimentally detected formate adsorbing on Pt electrodes at a bridge-bonded configuration during formic acid oxidation.⁸ Further, by potential step experiments they reported that the oxidation of HCOOH occurs dominantly through adsorbed formate whose decomposition to carbon dioxide is regarded as the rate-determining step.⁹ The adsorbed carbon monoxide holds the adsorption site and blocks the adsorption of formate then suppresses the decomposition of formate to CO_2 .⁹ To make their study more reliable, their point has been confirmed by isotope-labeled formic acids (H^{12}COOH and H^{13}COOH), that formic acid is oxidized to CO_2 through adsorbed formate and this direct path consumes most of the applied current.⁹ Also a mechanistic investigation of electrocatalytic oxidation of formic acid on Pd electrode in sulfuric and perchloric acids reported that by ATR-SEIRAS, it shows the adsorption of CO, bridge-bonded formate,

bicarbonate, and supporting anions on the electrode surface.¹⁰

To reveal the real story under the debate, a computational study on the mechanism of HCOOH decomposition and oxidation on Pd(1 1 1) surface has been conducted at density functional level

4.2 The adsorption of the intermediates

We explored the adsorption characteristics of HCOOH and H, HCOO, COOH which is involved in the mechanism of HCOOH decomposition and oxidation. They are examined with every possible adsorption site with all possible adsorption structure. The adsorption of H atoms on the Pd(1 1 1) surface has been discussed thoroughly, in this chapter, it won't be reiterated.

4.2.1 Formic acid (HCOOH)

Fig.4.1 Structure of the *cis*-HCOOH and *trans*-HCOOH, with their HOMO and LUMO presented.

There are 2 types of formic acid, namely *cis*-HCOOH and *trans*-HCOOH which has been showed in Fig.4.1 with their highest occupied molecule orbital (HOMO) and the lowest unoccupied molecule orbital (LUMO). We noted that the electrons are average located around the molecule. To have the optimized structure of the adsorbed formic acid, eight adsorption geometries are studied. The detailed structural and energetic information are summarized in Fig.4.2.

Fig.4.2a shows a hydrogen centered *cis*-HCOOH adsorption complex. The hydrogen atom getting closes and then interacts with a top Pd atom to a stable adsorption configuration where the Pd-H bond is 2.24 Å. The binding energy is 11 kJ/mol and in Fig.4.2b it shows a hydrogen centered *trans*-HCOOH adsorption complex. The hydrogen atom getting closes and then interacts with a top Pd atom to a stable adsorption configuration where the distance between the H atom and the surface Pd atom is 2.29 Å. The binding energy is 20 kJ/mol. Fig.4.2c shows the oxygen centered *cis*-formic acid with the Pd-O as long as 2.34 Å. And the binding energy is 2 kJ/mol. Fig.4.2d shows the oxygen centered *trans*-formic acid. The oxygen is interaction with the top later Pd atom (similar as the Fig.4.2c) and the Pd-O as long as 2.37 Å. The binding energy is 20 kJ/mol. Fig.4.2e shows the oxygen and hydrogen centered *trans*-HCOOH, the Pd-O bong is as long as 2.39 Å and the distance between the centered hydrogen and the Pd is 2.54 Å. The binding energy for this complex is 21 kJ/mol. Fig.4.2f is bioxygen centered *trans*-HCOOH. Here the two oxygen atoms are both interacting with the top layer Pd with the Pd-O (carboxyl group) as long as 2.45 Å and Pd-O (hydroxyl group) as long as 2.45 Å. The binding energy is 14 kJ/mol. Fig.4.2g and the Fig.4.2h and the planer adsorbed *cis*- and *trans*-HCOOH. Their binding energy is 5 and 8 kJ/mol, respectively.

Fig.4.2 The optimized adsorption configurations (in angstrom) and binding energy of formic acid when it binds to Pd(1 1 1) surface via various adsorption site. The binding energy (in kJ/mol) is shown in the parentheses. With the aim of clarity, the bottom two layers are not shown.

It is noted that the *trans*-HCOOH all show a higher binding energy than the *cis*-HCOOH with the same adsorption structure. The adsorption between the formic acid and the Pd surface is weak, we could not assign specific one as the most stable geometry. For the formic acid molecule shows weak interaction with the surface, as revealed by the low binding energy, the geometry has little effect on the binding energy. Then 4 geometries (Fig.4.2b~f) with higher binding energy are selected as the candidate who will participate the further decomposition.

4.2.2 Carboxyl group (COOH)

There are two types of carboxyl, namely COO-H_{up} and COO-H_{down}, have been examined as showed in Fig.4.3.¹¹ One is labeled as COO-H_{up} with its tailed hydrogen atom pointing upwards against the Pd(1 1 1) surface; the other is denoted as COO-H_{down} with its tailed hydrogen atom pointing downwards to the Pd(1 1 1) surface, as detailed showed bellow.

Fig.4.3 The structure of the carboxyl (COO-H_{up} and COO-H_{down}) with their binding energy (*E_b*, in kJ/mol) and HOMO and LUMO presented. The palladium surface is represented as the gray bar for clarity.

Fig.4.3 also shows the HOMO and LUMO of both the carboxyl structure. It is noted there is not much difference between the COO-H_{up} and COO-H_{down} form their HOMO and LUMO, so their stability are expected to changes slightly from the energetic point of view. This has been confirmed by the calculation adsorption energy. This is in

good agreement with the computational work by Lim *et al.* who claimed that the COO-H_{up} and COO-H_{down} shows similar stability on Pt(1 0 0) surface.¹¹

The most stable COO-H_{up} prefers to adsorb through the carbon center at the top site. The optimized adsorbed COO-H_{up} is planar which interact with the Pd(1 1 1) surface through a Pd-C bond as long as 1.99 Å. The angle of Pd-C-O (carbonyl group) and Pd-C-O (hydroxyl) are 125° and 121°, respectively. The angle of C-O-H (up) is 105°, as showed in Fig.4.3. The carboxyl group is reported to be most stable when it is absorbed through the top site.

4.2.3 Formate group (HCOO)

To have the most stable adsorption geometry of the formate, three configurations (mono-oxygen centered, oxygen and hydrogen centered, and bi-oxygen centered) are investigated. Fig.4.4 shows the structure of three types of formate, as well as their HOMO and LUMO. The electrons are concentrated around the oxygen indicating that the formate indicates to interact with the surface through the oxygen. Fig.4.4 also shows the optimized geometries with the specific binding energy of the bi-oxygen centered, monooxygen centered and oxygen and hydrogen centered formate adsorbing on the Pd(1 1 1) surface.

Bioxygen centered formate shows the strongest adsorption to Pd(1 1 1) surface ($E_b = 253$ kJ/mol). As showed in Fig.4.4, the electrons are concentrated around the oxygen atoms, two oxygen atoms get close to the surface together to make a better overlap of the orbitals. The most stable bioxygen centered formate is obtained when the two oxygen are binds to the top site of Pd with the Pd-O as long as 2.18 Å. During the

adsorption, the C=O bond is shrunk to 1.24 Å from 1.26 Å (free formate radical) and the O–C–O angle is adjusted to 130° from 113° (free formate radical in gas phase) to make a better overlap of the orbitals.

Fig.4.4 Three adsorption geometries of the adsorbed formate (from left to the right, there are bi-oxygen centered, monooxygen centered and oxygen and hydrogen centered formate) with their binding energy (in kJ/mol) and HOMO and LUMO presented. The surface is simplified for clarity.

For the monooxygen centered formate, it shows the highest stability when it is adsorbing at the *hcp* site with a Pd–O bond as long as 2.30 Å. The C=O (adsorbed to the surface) is slightly activated to 1.34 Å compared to the 1.26 Å in solo formate radical in gas phase. The C=O (adsorbed to the surface) is tilted, but not perpendicular, to the surface for a better interaction.

For the oxygen and hydrogen centered formate, the highest stability is obtained when the centered atoms (namely oxygen and hydrogen) are both adsorbed at the top

position. According to the HOMO and LUMO figure, there are barely electrons around the hydrogen atom. So the getting close of the hydrogen atom to the surface of the oxygen and hydrogen centered formate ($E_b = 171$ kJ/mol) does not improve the interaction compared to the monooxygen centered formate ($E_b = 182$ kJ/mol). The Pd–O and Pd–H bond is 2.10 Å and 2.34 Å, respectively. The hydrogen atom has a smaller Pauling radius than oxygen atom, but the H is more far away from the surface. It indicates a weaker interaction between the surface and the hydrogen atom. As showed in Fig.4.4, the electrons of the formate are concentrated around the oxygen atom, there are rare electrons around hydrogen which leads to the really week interaction between the hydrogen and the surface. With the existence of the surface, the carboxyl group (C=O) is elongated to 1.31 Å from 1.26 Å (free formate) and the C–H bond is elongated to 1.13 Å from 1.10 Å (free formate in gas phase).

4.3 The reaction mechanism of formic acid decomposition

To have a better understanding of which character is associate with the improvement of the DFAFCs, it is significant to explore the mechanism. In this chapter, we will discuss the reaction pathways in details.

4.3.1 The non-formate reaction pathway

Fig.4.5 summarized the reaction mechanism of formic acid decomposition on Pd(1 1 1) surface via non-formate pathway.

At beginning, the HCOOH molecule adsorb onto the surface via the H center (Fig.4.2b, $E_b = 20$ kJ/mol) or via oxygen and hydrogen center (Fig.4.2f, $E_b = 20$ kJ/mol).

For upper channel, the hydrogen adsorbed formic acid interacts with the surface and the activation of the C–H bond leads to the bond length elongation from 1.09 Å to 1.11 Å. And the C–H bond break encounter a reaction barrier of 69 kJ/mol and this will give out the product of adsorbed carboxyl and surface adsorbed hydrogen. The reaction energy for this step is exothermic by 18 kJ/mol. The adsorbed carboxyl dehydrogenate to the final product of carbon dioxide via the O–H bond break with a reaction barrier of 74 kJ/mol and the overall energy released is 43 kJ/mol.

Fig.4.5 The mechanism of formic acid oxidation on Pd(1 1 1) surface via non-formate pathway. For each specific reaction step, the activation energy (in kJ/mol) is labeled. The relevant geometry of the reactants as well as products is also attached. The surface and the products of H atom are omitted.

The lower channel shows the other non-formate pathway. For the formic acid molecule solve in the solution randomly, the molecule may adsorb on the surface with oxygen and hydrogen center. Its binding energy is same as the hydrogen adsorbed configuration, we suggest both adsorption configuration are possible. The hydrogen atom attract by the surface and with the C–H bond break, the carboxyl group adjust the position to get the optimized top-site carbon centered carboxyl. The reaction barrier for

this step is 45 kJ/mol. Then the carboxyl will react to the final product, carbon dioxide, via the O-H bond break.

This non-formate reaction pathway is in line with the literature. By first-principles calculations, the Neurock *et al.* have investigated the two possible reaction pathways for HCOOH decomposition on platinum surface through either adsorbed HCOO or COOH. From their DTF results, they conclude that adsorbed COOH plays a role of the intermediate.⁷

4.3.2 The formate reaction pathway

Fig.4.6 show the formate reaction pathway of the HCOOH decomposition on the Pd(1 1 1) surface with corresponding structure of the initial states and final states, reaction barriers presented for each specific step. The palladium surface as well as the products of the adsorbed hydrogen is not shown for clarity.

The formic acid may adsorb on the surface via the oxygen (carboxyl group) center, as showed in Fig.4.6 the upper panel, to give out energy of 20 kJ/mol. For the formic acid is a weak acid with the K_a equals to 1.8×10^{-4} . In the solution, the O-H bond will dissociate spontaneously. With the O-H bond break, the product is the oxygen centered formate. Because the oxygen centered formate is not the most stable configuration, it will further react to the final product or it will reconstruct to more stable configuration. For further reaction channel, the C-H bond is activated while the C-H bond of the adsorbed oxygen centered formate is elongated to 1.13 Å from 1.09 Å. The activation barrier of C-H bond break for this formate configuration is 73 kJ/mol. For the reconstruction channel, the oxygen centered formate may rotate to the oxygen and

hydrogen centered formate with a reaction energy of exothermic by 36 kJ/mol. And the reaction barrier of the C–H bond break for the oxygen and hydrogen center formate is 120 kJ/mol to the final product, carbon dioxide.

Fig.4.6 The mechanism of formic acid oxidation on Pd(1 1 1) surface via formate pathway. For each specific reaction step, the activation energy (in kJ/mol) is labeled. The relevant geometry of the reactants as well as products is also attached. The surface and the products of H atom are omitted.

This reaction pathway is agreed with the experiment. By ATR-SEIRAS, the formate adsorbed in a bridge-bonded configuration is detected during HCOOH oxidation on Pt electrodes.⁸ Osawa *et al.* further explored that carbon monoxide (CO) and formate were found to adsorb on the surface and potential step experiments revealed that the oxidation of HCOOH takes place dominantly through adsorbed formate and the rate-determining step is determined to be the decomposition of formate to CO₂.⁹ Adsorbed CO blocks the adsorption of formate and also suppresses the decomposition of formate to CO₂. This is confirmed by isotope-labeled formic acids (H¹²COOH and H¹³COOH) experiment which reported that formic acid is oxidized to CO₂ through adsorbed formate

and this direct path consumes most of the applied current.⁹ They also point out that a mechanistic study of electrocatalytic oxidation of formic acid on Pd in sulfuric and perchloric acids is reported. An ATR-SEIRAS experiment shows the adsorption of CO, bridge-bonded formate, bicarbonate, and supporting anions on the electrode surface. Adsorbed formate is detected only when formic acid oxidation is suppressed.¹⁰

4.3.3 formate as a site blocking species reaction pathway

The mechanism of formic acid oxidation on Pd(1 1 1) surface when the formate play the role of the site-blocking species is shown is Fig.4.7. For each specific reaction step, the activation energy (in kJ/mol) is labeled. The corresponding structure of the initial states and final states, activation energies (in kJ/mol) are also presented for each specific step.

Fig.4.7 The mechanism of formic acid oxidation on Pd(1 1 1) surface when the formate play the role of the site-blocking species. For each specific reaction step, the activation

energy (in kJ/mol) is labeled. The relevant geometry of the reactants as well as products is also attached. The surface and the products of H atom are omitted.

Figure.4.7 presents the reaction pathway of the HCOOH decomposition when formate plays the role as the site blocking species. There are three possible adsorption configuration of formate among which the bioxygen centered one has the strongest binding energy indicating the most stable state. The bioxygen-centered formate could be the product by O–H bond scission of the bioxygen centered formic acid. The reaction barrier for this step is 77 kJ/mol. There are another two pathways to lead to the bioxygen centered formate. One is the upper panel, the oxygen-centered formate reconstruct to the bioxygen centered formate and give out energy by 117 kJ/mol. The other is showed in the lower panel, the oxygen and hydrogen centered formate reconstruct to the bioxygen centered formate and release energy by 81 kJ/mol. The C–H bond is 1.09 Å in free radical while in the adsorbed formate (bioxygen-centered), the it is 1.10 Å. The similar bond length indicates that the surface does not active the C–H bond notability. The C–H bond break of bi-oxygen centered formate exhibits a high reaction barrier of 132 kJ/mol. The high reaction barrier made the bioxygen centered formate hard to react to the carbon bioxide. It is consistent with the reports by Neurock *et al.* which states adsorbed formate is a site-blocking spectator.⁷

4.4 Conclusions

Based on the controversy on the mechanism of HCCOH decomposition, we proposed three reaction pathways. We tentatively proposed that the controversy are

because the different reaction environment. For Osawa's experiment, they are using a strong acidic solution (concentration of H^+ is 1M) which will depress the dissociation of the formic acid molecule and will benefit the formic acid to adsorb to the surface as a molecule.⁸⁻¹⁰ The hydrogen adsorbed formic acid and the oxygen and hydrogen centered formic acid will lead the carboxyl by the C-H bond break and by a further O-H bond break to the final product of carbon dioxide. Another possible mechanism which may contribute to the current is the oxygen centered formic acid which will decompose via the O-H bond break with the assistance of the solution and a quick C-H bond break to the carbon dioxide. While Osawa reported that the formates are detected only when the reaction is suppressed.¹⁰ We suggest the reason that when the reaction is suppressed, the oxygen center formate and the oxygen and hydrogen centered formate take time to reconstruct to the bioxygen centered formate which will act as the site blocking species. For anjew, they claim that the adsorbed formate is not a reaction intermediate but a site-blocking spectator.⁷ The reason maybe they are using a less acid condition, then more formate are dissociated from the formic acid, and the formate radical are adsorbed on the surface through the most stable configuration which act as the site blocking species. Another reason may be due to the different technique they are using.

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Chapter 5. Electronic Characters of Pd(1 1 1) Surface with the 3d Transition Metal as the Sublayer Structure

The investigation on the mechanism of methanol and formic acid decomposition of Pd (1 1 1) surface have been carried out. With the aim of making the study more systematic, we will discuss the catalysis design. This chapter is focused on the study of the electronic characteristics of the Pd(1 1 1) surface with the 3d transition metal as the sublayer. We performed ab initio level quantum calculations to analyze the electronic characteristics of pure sublayer structured Pd(1 1 1) surface. Based on these studies, we hope to reveal how the sublayer structure effect the electronic characters of the Pd(1 1 1) surface.

5.1 Introduction

5.1.1 Bimetallic catalyst

The transition metals such as Pd, Pt or Rh serve as significant industrial catalysts.¹ Recent decades, a series of studies have been performed on bimetallic surfaces both theoretically²⁻⁴ and experimentally⁵⁻⁹. It is interesting that the bimetallic surfaces which include one of the late transition metals and a guest introduced metal exhibit promising chemical and catalytic properties. The extraordinary performance of the bimetallic system is different from neither the host nor the guest metal surface. The combinations of the host and guest metal may lead to an interaction between two significantly different *d*-

band occupation. The differently occupied d -bands results in a strong chemical interaction between the hosts and guest metal caused by significant d - d hybridization.^{10,11}

There are two major effects when a second metal is introduced to the host metal. One is the strain effect which shifts the d -band center (ϵ_d) upwards relative to the Fermi energy level (E_f) and strengthens the chemical interaction between the metal surface and the adsorbates.^{2,12} The other is the ligand effect which downshifts ϵ_d thus weaken the interaction of the adsorbates and metal surface and imply lower activation energy and as well as easier reaction.² Palladium, as an efficient catalyst, has been studied and used for decades. Recently, to improve catalytic activity, palladium-based alloy catalysts have been developed.^{2,13-19} Literatures have shown that the introduction of the guest metal into the host Pd surface can lead to the advantages of the ligand effect and the strain effect resulting in improved reactivity of the bimetallic catalysts.²

Compared to the corresponding micro-size particles, previous experiments have indicated that palladium nanoparticles present higher activity. However, the bimetallic systems, compared to mono-metallic palladium nanoparticles, are probably more interesting as the increase in the complexity of catalysts exhibit more probabilities to enhance catalytic performance. Recently, the works of both experiment and theory have revealed the development of nanosized palladium-alloys as the bimetallic catalysts. The bimetallic catalysts usually exhibit increased activity, selectivity and stability which are different from either of the constituent metals.^{16,17,20-23} The literatures have pointed out that the introduction of Fe, Co, Ni, Ti or Au atoms to the Pd system significantly enhance the activity of valuable catalytic reactions.^{16-19,21,23} For example, by the use of the lattice-strain effect of Co, an effective Pd-Co alloy catalyst has been designed for oxygen

reduction reactions.¹⁶ And it is revealed that Au could electronically influence the catalytic properties of Pd for the oxidation of alcohols.^{18,24}

5.1.2 Work function

Fig.5.1 The definition of the work function W . It is defined as the difference of energy level between the Fermi energy E_F and the external potential (solid curve) diverges at the atomic centers (black circles).

The work function of a metal is defined as the energy level difference between a neutral crystal and the same crystal with one electron removed in the condition of zero temperature and perfect vacuum. The work function was first defined in this way by Wigner and Bardeen in 1935.²⁵ The work function corresponds to the amount of energy required to extract one electron from the bulk or surface metal. For a metal, if E_N is the

initial energy of the metal and E_{N-1} that of the metal with one electron removed to a region of electrostatic potential V_e , we define

$$W = (E_{N-1} + V_e) \quad (5.1)$$

Work function is one of the most fundamental parameters of metal surface, and it is of great significance to lots of phenomena, such as physical and chemical adsorption, catalytical reactivity, thermionic emission and photoemission process. Langmuir was the pioneer who firstly measured the work functions. The measurement was performed to gain fundamental insights into the electronic properties of metals and to improve on electrolyte employed by the developing electric light industry. The quest for stable thermionic source and sensitive photodetectors then drove further research into work functions. With the years efforts, accurate values of the work functions for most metals in surface and bulk status have been established.²⁶ However, as a promising field, sublayer structured surface is till lack of systematic study both theoretically and experimentally. In this chapter, we study theoretically the work function of the Pd(1 1 1) with 3d transition metals as the sublayer.

At the surface, because the absence of the half the ionic neighbors, the equilibrium positions of the surface ions change and the interatomic forces are modified in consequence. The surface generally shows a modification of the inter-layer spacing at the surface which is known as the surface relaxation. And the surface relaxation makes the surface some advanced characterization such as the catalytical performance. For sublayer structured surface, the introduced of sublayer causes a relaxation of the surface, or even surface reconstruction. These rearrangements are expected to be revealed by the work function changes.

Since work function can affect the adsorption and the catalytical performance, in this chapter, we will explore the work function (Φ) in detail.

5.1.3 *d* band theory

d band model is simple but powerful to periodic the adsorption and reactivity trends.^{27,28} It links the electronic structure of a surface, more specifically the center of the *d*-band (ϵ_d), with the chemical reactivity of the surface. The surface is expected to bind the adsorbate more strongly if it is higher with ϵ_d (the Fermi level is set as standard level)

Hammer and Nørskov have developed the *d* band theory. They assumed that the trends in the chemisorption energy could be determined by the interaction of the adsorbate orbitals with surface *sp*- and *d*-bands.²⁸ For a single atom adsorbates, there will be only a single type of adsorbate orbital interacts with the surface. The model is expressed as the following equation:

$$E_{d-hyb} = -2(1-f) \frac{V^2}{|\epsilon_d - \epsilon_a|} + 2(1+f)\alpha V^2 \quad (5.2)$$

where E_{d-hyb} is the hybridization energy of the metal *d*-bands with the adsorbate orbital, f is the fractional coefficient corresponding the *d*-band filling, V is a Hamiltonian matrix element and it describes the coupling of the adsorbate orbital and the metal *d*-band, ϵ_a is the energy level of the adsorbate orbital and α is the constant that changes little between different system. Generally, the interactions of *sp*-bands of the metal surface with adsorbates rely on the nature of the adsorbate, thus ϵ_a is a constant. What's more, the *sp*-band interaction energies are constant which suggests that the difference of E_{d-hyb} for

specific adsorbates on different surface varies little to the corresponding difference of the chemisorption energies (E_{chem}). These phenomena, together with Equ. 5.2 come to the main story of the d -band model that is the changes in E_{chem} over various surface are simply related to changes in the ε_d . d -band model is powerful in predicting the chemisorption trends.

5.2 Results and discussion

The sublayer-structured alloys have shown promise for catalyst design. In this chapter, we investigate the electronic characterization of the Pd(1 1 1) surface with $3d$ transition metals (from d^1 to d^{10}) as the sublayer. By the study of the d band center, work function, we will discuss the probability of the Pd(1 1 1) surface with $3d$ transition metals as the sublayer to be the new catalyst.

Fig.5.2 The illustration of the Pd(1 1 1) slab with $3d$ transition metal as the sublayer structure (from side view).

Fig.5.2 shows the side view of Pd(1 1 1) surface with the sublayer structure. It is obtained by the replacement of the second top layer of the palladium atoms with the $3d$ transition metal atoms. The structural and the characteristic properties are summarized in

Table 5.1. The columns are listed as the 3d transition metals present in the periodical table. The introduced guest atoms affect the optimized lattice parameter as it showed in the Table 5.1.

The pure Pd(1 1 1) surface exhibits a lattice parameter of 2.75 Å (surface Pd–Pd bond as long as 2.75 Å). While with the effect of the sublayer structure (3d transition metal), the lattice parameter changes. The surface Pd–Pd bond is as long as 2.93 Å when Sc served as the sublayer. Then it decreases to the smallest value to 2.70 Å when the Mn served as the sublayer. After the lowest point, it increases gradually to 2.90 Å when the sublayer is Zn.

Fig.5.3 The variation of the Fermi energy level (in eV) of the Pd(1 1 1) surface with the effect of 3d transition metal as the sublayer.

Fig.5.3 shows the Fermi energy level (E_f) changes with the effect of the sublayer structure. When Sc atoms are placed at the sublayer, the surface gives out a Fermi energy level of -1.50 eV. While when the sublayer is the Ti and V atoms, the surface exhibits a Fermi energy level of -1.83 eV and -1.59 eV, respectively. Then the Fermi energy level decreases when the number of the electrons is increased until the Fermi energy gets the minimization of -2.16 eV when the Cu is the sublayer. Finally the Fermi energy increases a little to -2.02 eV when the sublayer is Zn.

Fig.5.4 The variation of the energy level of Pd (1 1 1) surface d band center (in eV) with the effect of 3d transition metal as the sublayer. The Fermi energy level is set as standard zero.

Fig.5.4 shows the variation of $\mathcal{E}_d$ of Pd(1 1 1) surface with the effect of sublayer structure. When the Sc and Ti atoms are the sublayer, the surface $\mathcal{E}_d$ is -2.77 eV and -2.76 eV, respectively. It is interesting to notice that the $\mathcal{E}_d$ shift up to the E_f level gradually with the electrons increase of the sublayer atoms. We notice that the surface $\mathcal{E}_d$ is -2.17 eV. The introduction of the guest metal adjusts the surface d band center both upwards and downwards.

Fig.5.5 The variation of the work function (in eV) of the Pd(1 1 1) surface with the effect of 3d transition metal as the sublayer.

The work function is an important quantity, which is at the basis of many interfacial phenomena, such as electronic transport, adsorption, and adhesion. Its control can lead to practical applications in many technological fields. For example, tuning the

work function can reduce the contact resistance between the anode and the Hall transport layers of organic light emitting diode devices,²⁹ control heterogeneous catalysis in water dissociation,³⁰ strongly enhance field emission currents,³¹ or lead to selective charging of adsorbed species, such as metal clusters.³²⁻³⁴

Fig.5.5 shows the variation of work function of Pd(1 1 1) surface with the effect of the sublayer. We notice that the modified work function is smaller than that of the pure Pd surface. Referring to its definition: the minimum amount of energy to remove one electron from the surface to immediately outside the surface, we conclude that with the effect of sublayer structure, the Pd(1 1 1) surface is more easy to give out electrons. When the Sc and Ti atoms are the sublayer, the work function of Pd(1 1 1) surface are 4.21 eV and 4.46 eV, respectively. It is interesting to notice that the Φ increase gradually with the increase of the electrons of the sublayer atoms.

Interestingly, the work function of the sublayer structured surface linearly increases while the sublayer metal's electronic configuration changes from s^2d^3 to s^2d^9 . This interesting phenomena is also found for the d -center of the sublayer structure-Pd(1 1 1) surface. As long as we could adjust work function and the energy level freely by the changing the sublayer metal, we tentatively propose that we could design the catalyst by adjust the surface work function to the desired value based on the different reactants.

5.3 Conclusions

The electronic characters of Pd(1 1 1) surface changes with the effect of the 3d transition metal as the sublayer (Table 1). We noticed that there are some liner relationships between the Fermi energy level, d band center and the work function of the

Pd(1 1 1) surface against the sublayer of the 3d transition metal from left hand site to the right hand site in the periodical table. The Fermi energy level of Pd(1 1 1) surface gives out a liner decrease from Cr ($3d^5s^1$) as the sublayer to the Cu ($3d^{10}s^1$) as the sublayer. The d band center and the work function of Pd(1 1 1) surface shows a liner increase from V ($3d^3s^2$) as the sublayer to the Cu ($3d^{10}s^1$) as the sublayer. Based on the definition of the work function and d band model theory, we propose design noble catalysts who could give out the optimized adsorption strength by the adjustment of the sublayer metals.

Table 5.1 The electronic characterization of the Pd(1 1 1) surface with 3d transition metal as the sublayer

sublayer	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
electronic configuration	$3d^1s^2$	$3d^2s^2$	$3d^3s^2$	$3d^5s^1$	$3d^5s^2$	$3d^6s^2$	$3d^7s^2$	$3d^8s^2$	$3d^{10}s^1$	$3d^{10}s^2$
Pd-Pd bond length (Å)	2.93	2.79	2.74	2.71	2.70	2.71	2.71	2.71	2.72	2.79
E_{fermi} (eV)	-1.50	-1.83	-1.59	-1.53	-1.62	-1.80	-1.94	-2.11	-2.16	-2.02
d -center (eV)	-2.77	-2.76	-2.94	-2.83	-2.69	-2.60	-2.38	-2.15	-1.83	-2.05
Φ (eV)	4.21	4.46	4.35	4.52	4.66	4.93	5.06	5.23	5.27	4.81

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Chapter.6 Summary and Future Work

6.1 Summary

Theoretical study on the mechanisms of Pd(1 1 1) surface catalyzed methanol decomposition on under neutral and alkaline condition have been carried out. Each possible species involving CH₃OH, CH₃O, CH₂OH, CH₂O, CHO, CO, H, OH, COOH and CO₂ is optimized to get the most stable geometry which turns out to agree well with the literature. Under neutral condition, the palladium demonstrate barely activity to methanol decomposition because the high reaction barriers block the reaction at the very first step. Under alkaline condition, the adsorbed hydroxyl assists the O–H bond scission of methanol ($E_a = 121$ kJ/mol under neutral condition and $E_a = 77$ kJ/mol under alkaline condition) to make the palladium more active than that under neutral condition. Under alkaline condition, the adsorbed OH assists methanol will decompose via the O–H bond scission to CH₃O which further decompose via a stepwise of C–H bond scission to CO. And the CO then combine with the adsorbed OH to carboxyl and the carboxyl leads to the final product carbon dioxide via O–H bond scission. In this mechanism, methanol methoxy, formaldehyde, formyl, carbon monoxide and carbon dioxide have been experimentally observed.

The DFAFC has attracted great interest in the past decades for they are regard as a promising alternative to H₂ and alcohol based fuel cells. However, the mechanism of HCOOH decomposition and oxidation is still suspended. Even the experimental results have given the controversial phenomena. Thus, as a following up, the mechanism of HCOOH oxidation on Pd(1 1 1) surface has been carried out. We have proposed three

reaction pathways. We tentatively proposed that the controversy are because the different reaction environment. For Osawa's experiment, they are using a strong acidic solution (concentration of H^+ is 1M) which will depress the dissociation of the formic acid molecule and will benefit the formic acid to adsorb to the surface as a molecule. For anjew *et al.*, they claimed that the adsorbed formate is not a reaction intermediate but a site-blocking spectator. The reason maybe they are using a less acid condition, then more formate are dissociated form the formic acid, and the formate radical are adsorbed on the surface through the most stale configuration which act as the site blocking species. Another reason may be due to the different technical they are using.

Finlay, to make this research more systematic and more practical, we have proposed a way to improve the catalytical performance of palladium electrode. With the aim of design novel catalyst through the sublayer structure Pd(1 1 1) surface, the analysis on the surface electronic structure have been carried out. It has been found out that the Fermi energy level, *d*-band center as well as work function of the Pd(1 1 1) surface is adjusted by the sublayer structure. Based on Brønsted–Evans–Polanyi (BEP) relation, Sabatier principle, work function theory and the d-band theory, we propose the probability of the new catalyst.

6.2 Future Work

Sabatier's principle is widely applied to surface reaction which stating that the effective catalyst adsorbs the reactants strongly but not so strongly that no products can desorb.¹ Furthermore, a number of surface reactions give out a linear Brønsted–Evans–Polanyi relation (BEP relation) between the reaction barrier energy and the reaction

energy, and even more interestingly, reactions in same category follow the similar BEP relation (as shown in Fig.6.1).²

Fig.6.1 The computational results of transition state energies (E_a) and dissociative chemisorption energies (ΔE_1) for N_2 , CO, NO, and O_2 on a set of transition metal surfaces. (both close packed and stepped surfaces).²

As long as the interaction between the adsorbates and the surface play an important role in the surface reaction, it is critical to understand the interaction between the adsorbate and the surface. It has been shown that for the adsorption on the metal

surface, the d -band model^{3,4} developed by Hammer and Nørskov, can forecast the strength of the chemisorption energies. The d -band model correlates the central moment of the metal surface's d -band with the reactivity of the surface. It has been used successfully to design novel metal surfaces for various catalytic reactions. In general, for a given adsorption geometry adsorbates bind to the surface of transition or noble metals more strongly if the surface atom is higher in ε_d energies (As showed in Fig.6.1).⁵ The model is very robust.

Fig.6.2 The variation of atomic adsorption energy (E_{chem}^{atomic} , in eV) with the effect of the d -band center (ε_d , in eV) of the metal surface.

As have we discussed above, the ε_d of the surface with give liner effect on the binding strength. The binding strength then directly affects the reaction barrier. We have revealed that the existence of the sublayer structure could adjust the ε_d of the surface

both upwards and downwards. It is expected that the existence of the sublayer structure could have an effect of the reaction barrier which is the focus of our future work.

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