

Theoretical Study on the Adsorption and Decomposition of Methanol over the PtCrCu (111) Surface

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Abstract

The density functional theory (DFT) and self-consistent periodic calculation were used to investigate methanol adsorption on the PtCrCu (111) surface. The adsorption energies, equilibrium geometries and vibration frequencies of thirteen type's methanol adsorption models on the PtCrCu (111) surface were predicted and the favorite adsorption model for methanol is the fcc-Pt2Cr. The strong anti-poisoning ability of the optimal adsorption model fcc-Pt2Cr has been found when the catalysts resistance to carbon monoxide (CO) was explored. Furthermore, after doping of Cr and Cu atoms in Pt-based catalysts energy band has been broadened and the original peak of the d-orbital for atom Pt which was close to the Fermi level disappears, these phenomena can explain why this new ternary alloy catalyst for the enhancement of electrocatalytic activity to some extent. The rate-determining step of possible decomposition pathway was investigated with transition state searching and the calculation results show that the activation barrier of O-H bond breaking with PtCrCu (111) ternary alloy catalyst is lower than that of O-H bond breaking without catalyzer in gas phase.

Keywords: Methanol, ternary alloy PtCrCu, DFT, electronic structure

1. Introduction

As fossil energy reserves decrease ceaselessly, all the countries have to put a lot of effort in order to find some new resources of energy to replace oil. Hydrogen energy which is a clean, high effective and renewable energy has absorbed much attention. As the key of hydrogen economy, fuel cell and its related fields have been a key point in the researches [1]. Proton exchange membrane fuel cell (PEMFC) has been regarded as an ideal power source because of its excellent performance with high specific capacity and low temperature (<100°C) [2-4]. As a new energy storage type, the proton exchange membrane fuel cell has great potential in the energy field because its advantages such as long life, pollution-free, high conversion efficiency. However, the intolerable cost and poor catalysis of the catalyst Pt-based currently used in PEMFC, together with other technical problems, block PEMFC from popularization [5]. One of the main barriers for the commercialization of PEMFC is the high loading of Pt and low utility of it. How to reduce the amount of platinum that is a rare resource used and improve catalytic ability has become a great challenge already for PEMFC. Hence, it is necessary to prepare high-efficiency supports to decrease the dosage of the novel metal

Pt, which is one of the current research hotspots in fuel cell. Many catalysts candidates, such as metal oxide and metalloporphyrin were used as catalyst in PEMFC to replace metal Pt. Unfortunately the catalytic capabilities of these new catalysts are lower than that of pure Pt and due to the factors within catalysts themselves the application of these new catalysts are also limited. Another way to approach the problem is by mixing different transition metals with metal Pt to form alloys, which have mainly focused on Pt binary alloy, Pt ternary alloy and quaternary alloy. A range of different Pt binary alloys Pt-M (M=V, Mn, Cr, Ni and Cu) was investigated by T. Ghosh' group [9], indicating that catalysis to methanol's electro-oxidization-reaction of Pt metal has been greatly improved after doping Cu, Ni, Cr and Mn respectively, especially the catalytic capability of Pt-Cr was almost 20 times higher than that of pure Pt-base. Pt-Cu was prepared into core-shell structure by Strasser [10] to accelerate the sluggish kinetics of oxygen reduction reaction (ORR) in fuel cell systems and their results show that the elastic strain force which comes from low coverage of Pt has made the energy band shift to the lower-energy state, as a result the adsorption of intermediate decreases and the catalysis of catalyst enhances. Some of the recent insights into the catalytic properties of ternary catalysts prepared by molecularly-engineered synthesis and thermochemically-controlled processing, focusing on oxygen reduction in fuel cells [11-16]. Most of the findings reveal that the catalytic capability of Pt ternary alloy is superior to that of Pt binary alloy and commercial electro-catalyst Pt/C and the activity and stability of ternary alloy can be easily tailored by modifying structural and compositional parameters. Therefore, the research of Pt ternary alloy and Pt ternary alloy electro-catalyst supported on carbon has profound effect.

The development of quantum chemistry theory of efficient ORR catalysts provided progress in our understanding of ORR activity and yielded promising catalyst materials for fuel cell experimentalists. Interatomic interactions in Pt/C and Pt-Fe/C alloy catalyst were studied by ab initio method and the B3LYP functional of density functional theory (DFT) [17], the results show that doping atom metal Fe could improve the activity and stability of the catalyst effectively. We did a lot of work to research on the binary alloys supported by carbon Pt-M/C (M= Fe, Co, Ni, Mo) using DFT [18-21] and the model calculation and predication show good agreement with the experimental results which indicates that this model and method could be applied to explore other type of electro-catalyst, such as Pt binary alloy, Pt ternary alloy.

Pt ternary alloy electro-catalyst Pt-Pd-Cu with excellent performance was prepared by Jaeyune Ryu and his co-workers [23]. This new ternary alloy catalyst exhibited enhanced ORR performances compared to commercial Pt/C, but also they displayed outstanding durability. However, because of the high-cost production of the noble metal platinum and palladium, the commercialization of PEMFC using this new alloy electro-catalyst is hard to realize in PEMFC. Theoretical studies of fuel cell catalysts focused on the surface of Pt-M and Pt-M/C in the past, however there was few report about Pt ternary alloy by using the method of quantum-chemistry calculation. The transition metallic chromium has been selected to replace metal palladium by the same proportion due to its good properties and low price. This paper studied the methanol adsorption and decomposition on the Pt-Cr-Cu (111) based on the quantum chemical calculation method. Moreover, the electronic structure of ternary alloy was calculated from the microcosmic view, aiming to predict the properties of Pt-Cr-Cu alloy and provide useful information to design new fuel catalyst with low cost but good performance.

2. Computational Models and Methods

In this study, DFT and self-consistent periodic calculation were used to simulate the oxidation of methanol over the surface of Pt-Cr-Cu ternary alloy. The adsorption energies, equilibrium geometries and frequency analysis of thirteen models on Pt-Cr-Cu (111) (top-Pt, top-Cr, top-Cu, bridge-Pt₂, bridge-PtCr, bridge-PtCu, bridge-CrCu, hcp-Pt₂Cr, hcp-Pt₂Cu, hcp-PtCrCu, fcc-Pt₂Cr, fcc-Pt₂Cu, fcc-PtCrCu) have been predicted and compared. In addition, the electronic structure of Pt-Cr-Cu (111) and possible decomposition pathway of methanol on the surface of this ternary alloy are researched and analyzed. The similar model 3×3 super cell that has been used to explore the adsorption and decomposition of methanol over the Pt binary alloy supported by carbon [18-21] is also selected to calculate this system. We find that the different of the number of thickness has only a little unfavorable effect on the adsorption energy of methanol, but the configuration and relative stability of adsorptive materials remain the same. Considering precision and efficiency, three slabs model is chosen to investigate Pt-Cr-Cu (111) surface. In this research, the Pt-Cr-Cu 2:1:1 catalyst is prepared because the Pt-Pd-Cu 2:1:1 catalyst has highest performance in Ryu's experiment [23].

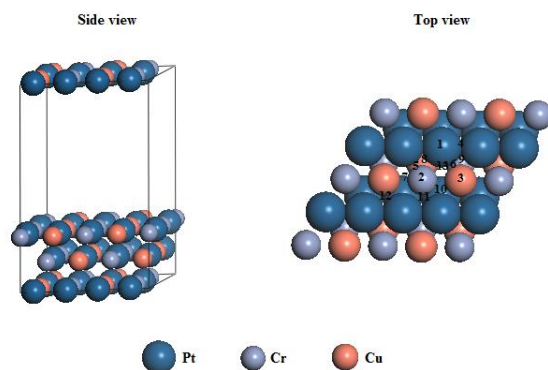


Figure 1. (Left) Side View of the PtCrCu(111) Surface with the Unit Lattice. (Right) Illustration of Adsorption Sites on the PtCrCu(111) Surface in the Top View (1.top-Pt; 2.top-Cr; 3. top-Cu;4.bridge-Pt₂; 5.Bridge-PtCr; 6.Bridge-PtCu; 7. Bridge-CrCu; 9.hcp-Pt₂Cr; 10.hcp-Pt₂Cu; 11.fcc-Pt₂Cr; 12.fcc-Pt₂Cu; 13.fcc-PtCrCu)

The side view and top view of Pt-Cr-Cu (111) surface are shown in Figure 1; add a vacuum with a thickness of around 15 Å. In order to make atoms of the top metal surface can freely move, the surface relaxation is considered and the lower two layers are fixed. The finite model has been built in this study could save a large amount of computing time and give reasonable results [24]. Double numeric with polarization (DNP) has been taken to calculate [25] that atom C, O and H are fully optimized by using all electron group and Effective core potentials (ECP) have been employed for all the metal atoms [26]. The generalized gradient approximation (GGA) with Perdew-Wang (PW91) [27, 28] exchange correlation function is selected in the DFT calculations. Fine grid mesh points are employed for the matrix integrations. Meanwhile transition state is confirmed by the method of linear synchronous transit (LST) and quadratic synchronous transit (QST) [29]. Adsorption energy values are calculated by

$$E_{\text{ads}} = E_{\text{methanol}} + E_{\text{PtCrCu}} - E_{\text{methanol+PtCrCu}}$$

Where the subscripts methanol and PtCrCu denote the energies of CH₃OH and PtCrCu denote the energies of PtCrCu respectively before adsorption. Furthermore, the subscript methanol+ PtCrCu refers to the energy of the adsorbed system. All calculations have been performed using DMol³ code [30, 31] as implemented in Accelrys Materials Studio 4.0.

3. Results and Discussion

3.1. Process of CH₃OH and CO Adsorption on the PtCrCu (111) Surface

The large numbers of research indicated oxygen termination was adsorbed first on the surface of catalyst during the electrochemical reaction of methanol on the catalyst surface, such as Pd (111) [32], Ag (111) [33] and Cu (111) [34], next hydroxymethyl intermediates could be formed. In the paper by Desai *et al.* [35], they modeled the dehydrogenation of methanol over the Pt (111) surface using DFT. They modeled seven different intermediates (methanol, methoxide, hydroxymethyl, formaldehyde, formyl, carbon monoxide, and hydrogen), and found that hydroxymethyl is a strong potential reactant intermediate and the adsorption activation of hydrogen on this surface is the rate-determining-step during the electro-catalytic reaction of fuel cells. Therefore, in this work we optimized the equilibrium geometries of CH₃OH on thirteen types of models of PtCrCu (111) surface using the mode of oxygen termination adsorption in which the O-C bond of original structure situates vertically over the catalyst surface as shown in Figure1, showing that the structure of methanol is inclining during the process of adsorption, which have occurred in the theoretical study on the adsorption of methanol over Pt-Fe (111)/C [18]. To study the structural change of adsorbed CH₃OH is our major work. Partial geometrical parameters and vibrational frequencies of CH₃OH are shown in Table 1 and Table 2, it is obvious to see that the calculation results of free CH₃OH are in agreement with the available experimental results[36, 37], indicating that the methods and modes we have chosen are reasonable. From Table 2, we can find out that the best adsorption model for methanol is fcc-Pt₂Cr by comparing the adsorption energies of methanol on thirteen types of model; the top-Pt is the next, but the most unstable one is bridge-Pt₂. There is little surface relaxation and reconstruction in the process of adsorption, indicating that the structures of substrates in this research is stable as well as reasonable. The structure of methanol molecule changes obviously during the process of adsorption, that is, hydrogen atoms from the hydroxyl direct towards the PtCrCu (111) surface to different degrees and the length of O-H elongate as well as O-C. Furthermore, the results show that the vibrational frequencies of O-H and O-C are red shifted in the equilibrium adsorption models and the change of top-Pt, top-Cu and fcc-Pt₂Cr distracts were the most obvious in thirteen adsorption models.

Taking the fcc-Pt₂Cr adsorption model as an example, the bond length of O-H is 0.0809nm longer than that of the free one, and the C-O bond is elongated by 0.0026nm, but the bond length of C-H has changed only 0.0007 nm, and ∠C-O-H increases about 4.8°. Obviously, the changes of the bond lengths of the O-H bond are very evident, but the bond lengths of the C-H has changed little, indicating that O-H bond is weaken at the initial stage of adsorption and easy to break. On the other hand, the decrease of 502.3 cm⁻¹ and 83.6 cm⁻¹ for O-H and C-O, respectively according to frequency analysis. The red shift reveals that the corresponding bonds are weakened, the O-H bond has the strongest active degree, and the next one is the C-O bond, but the

frequency of the C-H bond changes little. The change of the other models has the similar tendency, namely, the intensities of O-H bond is weakened at an early stage of adsorption.

Table 1. Geometrical Parameters of CH₃OH and Quilibrium Adsorption on Pt-Cr-Cu (111) Surface

Adsorption site	R(O-H)/nm	R(C-O)/nm	R(C-H)/nm	∠C-O-H/(°)
top-Pt	0.1007	0.1450	0.1107	110.9
top-Cr	0.0997	0.1447	0.1105	108.5
top-Cu	0.1010	0.1446	0.1103	108.3
bridge-Pt ₂	0.0994	0.1445	0.1102	107.7
bridge-PtCr	0.1005	0.1449	0.1106	109.8
bridge-PtCu	0.0989	0.1444	0.1104	108.3
bridge-CrCu	0.0995	0.1446	0.1106	108.7
hcp-Pt ₂ Cr	0.0990	0.1447	0.1107	108.6
hcp-Pt ₂ Cu	0.1003	0.1448	0.1105	109.7
hcp-PtCrCu	0.0989	0.1451	0.1106	110.6
fcc-Pt ₂ Cr	0.1016	0.1453	0.1109	112.3
fcc-Pt ₂ Cu	0.1000	0.1448	0.1105	109.8
fcc-PtCrCu	0.0987	0.1450	0.1103	109.4
CH ₃ OH	0.0969	0.1427	0.1102	107.5
(expert) ²⁹	0.0964	0.1431	0.1100	108.0

From Table 1, we can find out that the favorable adsorption model for methanol is the fcc-Pt₂Cr (E_{ads}=327.47kJ·mol⁻¹) by comparing the adsorption energies of methanol on thirteen types of models, but the most unstable model is bridge-Pt₂ (E_{ads}=319.62kJ·mol⁻¹), and accordingly the adsorption energy differs pretty small. The adsorption energies of all the thirteen adsorption models that range from 320 ~ 330 kJ·mol⁻¹ are so much higher than that of CO on Pt (111) surface (the largest adsorption energies is 63.7kJ·mol⁻¹ [38]). It indicates that the new catalyst PtCrCu(111) possesses the high adsorptivity for the adsorption of methanol, which can increase the reaction rate of the rate-determining step greatly, as a result, the performance of fuel cells can be improved to some extent. Meanwhile the anti-poisoning ability of the anodic electrocatalysts for methanol oxidation is the key in direct methanol fuel cells. Therefore, as a continuation of our investigation, the adsorption energies of CO on PtCrCu(111) surface have been summarized in Table 1, all of which are lower than that of CH₃OH on corresponding models, indicating that the catalyst PtCrCu(111) has some anti-poisoning ability. Those calculations also demonstrate that the adsorption energies of carbon monoxide over the two pure platinum adsorption sites (top-Pt and bridge-Pt₂) are larger, they are 298.58 and 299.47 kJ·mol⁻¹ respectively; but the adsorption energies of methanol over these same sites are 327.31 and 319.62 kJ·mol⁻¹, indicating that the adsorption energies are close to each other when the two adsorption substances are adsorbed on these same sites without obvious anti-poisoning ability for carbon monoxide. Furthermore, top-Cr, top-Cu, bridge-PtCr, bridge-PtCu, hcp-Pt₂Cr, fcc-Pt₂Cu and fcc-PtCrCu are in the group 2, the adsorption energies of carbon monoxide over them are about 200 kJ·mol⁻¹, which are 120 kJ·mol⁻¹ lower than that of CH₃OH on corresponding models but 40 kJ·mol⁻¹ higher than that of CO on pure Pt(111). The

third group of sites, including bridge-CrCu, hcp-Pt₂Cu, hcp-PtCrCu and fcc-Pt₂Cr, the adsorption energies of carbon monoxide over them are 116.67, 100.14, 115.28 and 99.72 kJ·mol⁻¹. This group is completely different that the other two groups, the adsorption energies of carbon monoxide have decreased significantly comparing with pure Pt (111) catalyst. The results of the calculation also show that fcc-Pt₂Cr, the best adsorption model for methanol, has the lowest adsorption energies of carbon monoxide, indicating that this model is an ideal catalytic site, not only with superior adsorption capacity of methanol but also strong anti-poisoning ability for carbon monoxide.

Table 2. Adsorption Energies and Vibrational Frequencies of Adsorption of CH₃OH on Pt-Cr-Cu (111) Surface

Adsorption site	E _{ads-CH₃OH} / (kJ·mol ⁻¹)	E _{ads-CO} / (kJ·mol ⁻¹)	v(O-H)/cm ⁻¹	v(C-O)/ cm ⁻¹
top-Pt	327.31	298.58	3253.8	980.2
top-Cr	325.68	199.98	3269.3	1004.7
top-Cu	322.25	200.43	3276.6	1006.1
bridge-Pt ₂	319.62	299.47	3281.9	1005.3
bridge-PtCr	326.66	197.56	3263.4	985.3
bridge-PtCu	320.47	199.31	3280.7	1009.2
bridge-CrCu	324.06	116.67	3271.8	1003.0
hcp-Pt ₂ Cr	323.51	199.28	3275.3	1013.1
hcp-Pt ₂ Cu	326.25	100.14	3265.2	994.9
hcp-PtCrCu	327.14	115.28	3255.1	981.5
fcc-Pt ₂ Cr	327.47	99.72	3248.4	971.0
fcc-Pt ₂ Cu	326.06	199.76	3266.7	992.4
fcc-PtCrCu	326.68	196.81	3264.0	986.1
CH ₃ OH	—	—	3750.7	1054.6
(expert) ²⁹	—	—	3682	1026

3.2. Electronic Structure

Natural population analysis (NPA) calculation is a common method of charge population analysis at the present, but there are some problems when this method is used to calculate transitional metals and some of heavy metals [39]. Taking into account the cost and precision of calculation, Milliken population analysis has been selected to study charge transfer trend of methanol, as shown in Table 3. It is obvious see that methanol has taken the positive electrical charge in the adsorption system, indicating that the charges have transferred from CH₃OH to the PtCrCu (111) surface already in the process of adsorption. Moreover, both C and O atoms adopt the hybrid of sp³ in free methanol molecule, and atom O takes two pairs of solitary electrons. There is 6 eV difference between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of methanol according to the calculational results of frontier molecular orbitals. The LUMO of methanol belongs to σ*-orbital with high energy so that it hardly obtains charge from the alloy surface. The HOMO of methanol belongs to the bonding-orbital, which is in the full-filling state, the component of which mainly from the two pairs of solitary electrons of atom O. The methanol molecule reacts on the surface of crystal substrate mainly by the two pairs of solitary electrons of atom O. As we know, the electronic structures of Pt, Cr and Cu are 5d⁹6s¹, 3d⁵4s¹ and 3d¹⁰4s¹

respectively. For one thing, the $3d$ orbital energy of the dopant atoms is lower than that of $5d$ orbital in Pt atom; secondly, because of the doping of Cr atom in catalyst, the whole the vacancy rates of d -orbital have increased; what is more, there is the high symmetry between the HOMO of methanol and the LOMO of catalyst substrate. As a result, the two pairs of solitary electrons of atom O may prefer to transfer to the d orbital of the alloy surface to improve the bonding capability as well as adsorption energy. On the other hand, the stability of catalyst can also be further enhanced to some extent due to the half full-filling state and full-filling state of d orbital in Cr and Cu atoms respectively.

Table 3. Mulliken Population Analysis for CH₃OH on Pt-Cr-Cu (111) Surface Adsorption System

adsorption site	q _O	q _{H1}	q _C	q _{H2}	q _{H3}	q _{H4}	q _{CH₃OH}
top-Pt	-0.484	0.318	-0.008	0.117	0.121	0.119	0.183
top-Cr	-0.497	0.295	-0.008	0.123	0.121	0.119	0.153
top-Cu	-0.493	0.294	-0.011	0.119	0.119	0.118	0.146
bridge-Pt ₂	-0.495	0.293	-0.012	0.119	0.118	0.122	0.145
bridge-PtCr	-0.489	0.306	-0.009	0.121	0.119	0.118	0.166
bridge-PtCu	-0.488	0.289	-0.012	0.123	0.118	0.118	0.148
bridge-CrCu	-0.496	0.293	-0.008	0.123	0.120	0.119	0.151
hcp-Pt ₂ Cr	-0.498	0.293	-0.008	0.122	0.119	0.123	0.149
hcp-Pt ₂ Cu	-0.493	0.299	-0.009	0.123	0.119	0.122	0.161
hcp-PtCrCu	-0.488	0.312	-0.009	0.124	0.118	0.119	0.177
fcc-Pt ₂ Cr	-0.482	0.321	-0.008	0.123	0.119	0.119	0.193
fcc-Pt ₂ Cu	-0.495	0.297	-0.007	0.122	0.118	0.125	0.155
fcc-PtCrCu	-0.491	0.299	-0.012	0.119	0.121	0.123	0.160
free CH ₃ OH	-0.555	0.267	0.063	0.088	0.068	0.069	0.000

The total density of states (TDOS) of Pt (111) and PtCrCu (111) are shown in Figure 2. As you can see in this figure, the range of energy band is $-0.521 \sim 0.05029$ Ha over the pure Pt (111) surface, but the energy band of catalyst surface has widened about 1.6424 eV after being doped with Cr and Cu atoms, which helps to explain why the activity of catalyst for methanol has been enhanced in the ternary alloy PtCrCu (111). Figure a, b and c in Figure 3 respectively illustrate the partial density of states (PDOS) of Pt, Cr and Cu atoms for PtCrCu (111). The d -orbital of Pt atom has provided most of electrons to the DOS of pure Pt (111) which is close to the Fermi level, followed by p -orbital of Pt atom [40]. After being doped, the d -orbital of Pt atom have made little contribution to the DOS, but some of the other orbits including the s -orbital of Pt atom, s and p orbital of Cr atom and p and d orbital of Cu atom have make an important role in the DOS near the Fermi level. For Pt atom, the peak of d -orbital near the Fermi level has disappeared possibly resulting from the electrons in d -orbital of Pt transfer to the half full-filling state of 3 d -orbital in Cr atom, which can further benefit to the transfer of electrons from methanol to d -orbital of Pt, with a corresponding increase of binding interaction. And based on these results, the phenomenon that the adsorption energies of methanol over the ternary alloy PtCrCu (111) surface have been increased obviously can be explained well.

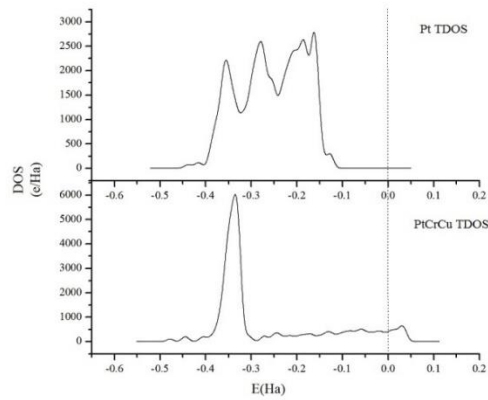


Figure 2. Total Densities of State (DOS) for the Clean Pt (111) and PtcrCu (111) Surfaces

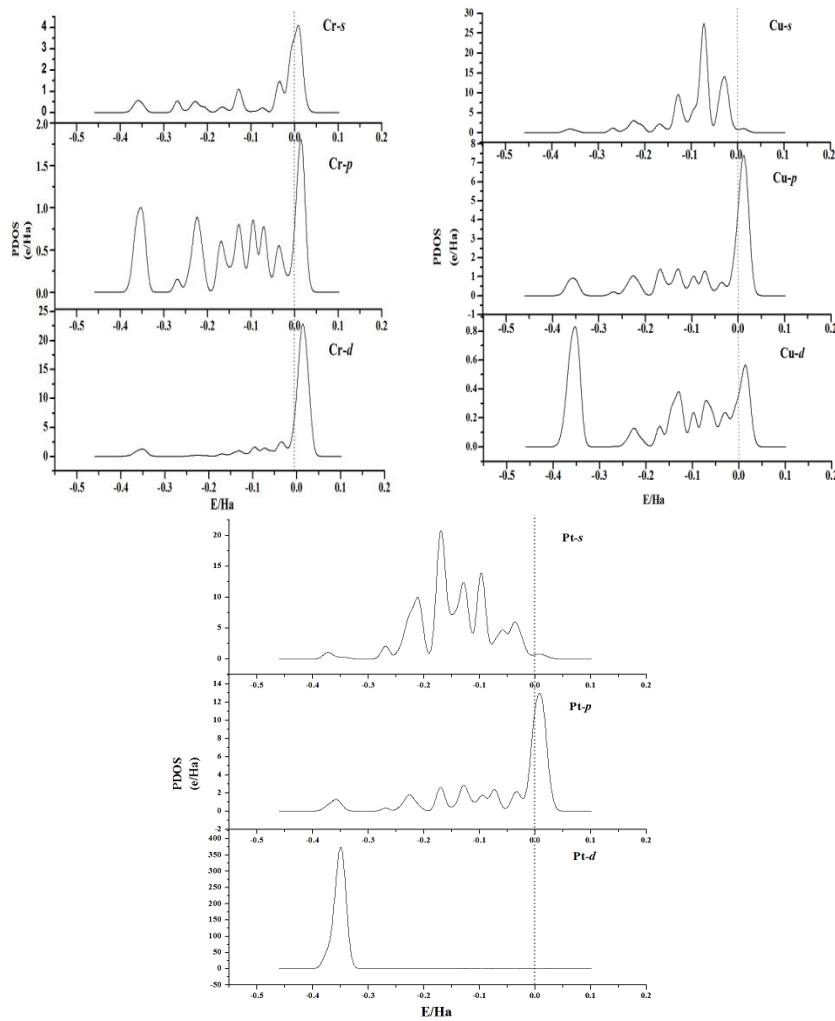


Figure 3. Partial Density States of atom Pt, Cr and Cu in PtCrCu (111) 3.3 Dissociation of Methanol over the PtCrCu (111) Surface

Wang's group had found that the mechanism of decomposition for methanol is the same even over the surface of different pure metals [41], which can be expressed as, and then. Furthermore, the first step is the rate-determining step of the decomposition for methanol due to lower energy barrier than that of the second step. The same conclusion could be obtained by using the same mechanism to investigate the decomposition of methanol over the PtCrCu (111) surface in this research.

Based on the above discussion, it is clear that fcc-Pt₂Cr model of PtCrCu (111) surface is favorable for the adsorption of CH₃OH to occur. The fcc-Pt₂Cr adsorption state can be used as the reactant of the dissociation process for methanol. We continue to calculate the adsorption of CH₃O and H on the PtCrCu (111) surface and it turns out that the best adsorption model for CH₃OH is hcp-Pt₂Cu and that of H is the top-Cr model. Accordingly, putting CH₃O and atom H on the PtCrCu (111) surface which is in co-adsorption state to optimize is reasonable, and the stable geometry is obtained as the product of dissociating methanol over the PtCrCu (111) surface, as shown in Figure 4.

Preliminary transition-state geometries are obtained using the integrated linear synchronous transit/quadratic synchronous transit (LST/QST) method [29]; and the computational details used are the same as that of the adsorption process. In dissociation the H-O bond is broken, then atoms H and O move towards the surface of crystal substrate, respectively. The result shows that CH₃O tends to the hcp-Pt₂Cu site of the surface, and atom H moves from the fcc-Pt₂Cr site to the top-Cr site, which is consistent with the experiments [22]. The distances of H and O vary from 0.1016 nm to 0.3374 nm in the process of adsorption, the nearest distance between O and the surface is 0.2458 nm and that of C and the surface is 0.3465 nm, which are shorter than the original distance of these (0.2673 nm and 0.3512 nm respectively). These results reveal that the CH₃O is more close to the surface of catalyst in the transition state, which benefits to the formations of O-Pt-Cr-Cu bond and H-Pt-Cr-Cu bond and enables the transition state to exist stably on the surface of substrate. Meanwhile, this process displays high similarity to the decomposition of methane over the surface of pure metal as well as the decomposition of methanol over the surface of binary alloy supported by carbon [42]. Both O-Pt-Cr-Cu and H-Pt-Cr-Cu bond have formed, along with the breaking of O-H bond. The energies given out by the formation of new bond have supplied the energies needed in the broken process, and the activation barrier only to be 297.2 kJ·mol⁻¹, which is 132.8 kJ·mol⁻¹ lower comparing with that of experimental result 430.0 kJ·mol⁻¹[36], showing that this process of O-H bond breaking is favorable to occur over the PtCrCu (111) surface. Furthermore, the same method is used to calculate the second step of the decomposition for methanol over the same catalyst, and the activation barrier of which is only 53.6 kJ·mol⁻¹(only 1/5 of the first step), so it is not the rate controlling step of dissociation reaction.

4. Summary

The microcosmic reaction mechanism of the methanol adsorption on PtCrCu(111) surface has been investigated by DFT. The favorable adsorption occurs at the fcc-Pt₂Cr, where the adsorption energy is higher than that of the others and reaches to 327.47 kJ·mol⁻¹, and the bridge-Pt₂ model ($E_{ads}=319.62\text{kJ}\cdot\text{mol}^{-1}$) is least stable, all of their adsorption energies are so much higher than the maximum adsorption energy on pure Pt (111) surface. In the process of adsorption, the length of O-H has prolonged, and the vibrational frequency of O-H bond is likely to generate Einstein shift phenomena according to frequency analysis. These results show that O-H bond has been activated

already. The adsorption capacity of methanol is higher than carbon monoxide basing on the adsorption energies of carbon monoxide, and fcc-Pt₂Cr is an ideal catalytic site with the lowest adsorption energy of carbon monoxide. The energy band of doped system has been broadened and the original peak of the *d*-orbital for atom Pt which was close to the Fermi level disappears, these phenomena can explain why this new ternary alloy catalyst for the enhancement of electrocatalytic activity to some extent. The broken energy of O-H bond with PtCrCu(111) catalyst is 132.8 kJ·mol⁻¹ lower comparing with conditions without any catalyst, this result indicates that the new catalyst is conducive to the procedure of dehydrogenation. In conclusion, PtCrCu (111) ternary alloy is good catalyst for the catalytic oxidation of methanol and it will have huge potential to become the catalyst of fuel cell by improving and modifying its structure to reduce the activation energy of rate controlling step and the toxic effects of CO.

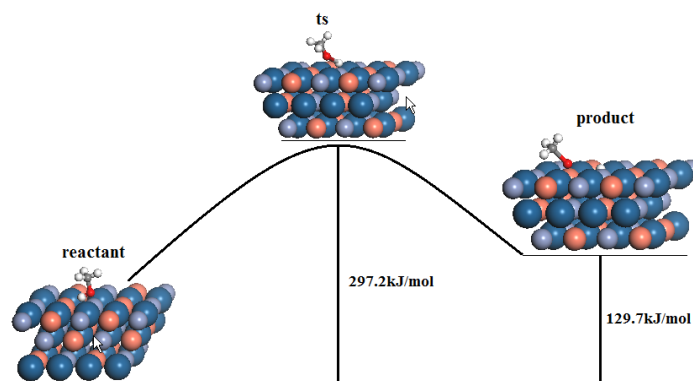


Figure 4. Dissociation Pathway for CH₃OH on the PtCrCu (111) Surfaces

Acknowledgments

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