

DFT study on the effect of electric field on the adsorption of methanol on Pd(1 1 1)

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Abstract. Density functional theory (DFT) calculations for the methanol oxidation reaction (MOR) has attracted much more attention than ever before, since the mechanism of methanol dehydrogenation is very important in direct methanol fuel cell (DMFC). Herein, methanol adsorption on Pd(111) with different electric field intensity (0.000, 0.0010, 0.0025 and 0.0050 au) were studied with DFT calculations. The results showed that methanol may adsorb on the Pd(1 1 1) either through the methyl or the hydroxyl of methanol in the absence electric field, since the two adsorption configurations share the similar adsorption energy. However, along with the increase of the electric field intensity, the angles formed by C-O bond axis and Pd(1 1 1) became gradually smaller, and it is only 1.9° when the electric field intensity value is 0.0050 au for the methyl case; while it kept at $35 \pm 5^\circ$ for the hydroxyl case. The methanol molecule was not activated in the reported electric field.

1 Introduction

Considering the environmental pollution and energy crisis, various energy storage and conversion systems have been developed. Methanol has attracted much attention because of their huge potential application in the fuel cells [1, 2]. DMFC which is based on either methanol decomposition or methanol steam reforming has aroused extensive research interest, since it is substantial efficiency, user-friendly and portable, low operating temperature, and high power density [3, 4].

Currently, the methanol decomposition on different metal catalysts, such as Pd [5, 6], Pt [4, 7], Rh[8] has been extensively investigated. The Brønsted-Evans-Polanyi (BEP) rules which describe the relation between reaction energy and energy barrier identified the C-H and O-H bond scissions as being more competitive than the C-O bond scission. Wu [9] found that the MOR proceeds through $\text{CH}_3\text{OH} - \text{CH}_3\text{O} - \text{CH}_2\text{O} - \text{CHO} - \text{CO}$. The scission of C-H bond likely to occur for CH_3OH and CH_2OH , and the O-H bond cleavage likely to occur for CHOH were also reported. While most of the DFT calculations omit the effect of electric field. However, electrocatalysis is a kind of catalytic to accelerate the charge transfer reaction between electrode and electrolyte. Its typical characteristic is that the electrocatalytic reaction is not only related to the activity of the electrocatalyst, but also to the electric field of the double layer. Because of the high electric field intensity in the double layer, it has obvious activation effect on the molecules or ions participating in the electrochemical

reaction, which greatly reduces the activation energy required for the reaction. Therefore, most electrocatalytic reactions can be carried out at temperatures much lower than the usual chemical reactions. Considering the fact that the exact MOR always starts from the adsorption of methanol on the surface of catalysts. The methanol adsorption on the Pd(111) surface in various electric field (0.000, 0.0010, 0.0025 and 0.0050 au) have been calculated in this paper.

2 Computational models and methods

Three layers (2×2) Pd(1 1 1) periodic slab model, in which the lower two layers were fixed at their bulk positions and the top layer was relaxed was chosen for the calculations. The coverage of methanol adsorbed on the Pd(1 1 1) surface was 1/4 monolayer, the thickness of the vacuum was set to be 11.23 Å which is 5 times of the distance between two close Pd-Pd layers. All the calculations were performed with density functional theory under the Dmol³ simulation package, and the PW91 method under generalized gradient approximation (GGA) was used to calculate the exchange correlation energy. The DFT Semi-core Pseudopotentials was chosen to describe the Pd atoms. The k point of Brillouin zone was set to be $4 \times 4 \times 1$, and the double numerical basis plus d class extended orbital was used. The adsorption energy of methanol (E_{ads}) was calculated according to equation (1):

$$E_{ads} = E_{\text{methanol/Pd}} - (E_{\text{methanol}} + E_{\text{Pd}}) \quad (1)$$

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where $E_{\text{methanol}/\text{Pd}}$ is the total energy of the methanol adsorbed on Pd(1 1 1) surface, E_{methanol} is the energy of methanol molecule, and E_{Pd} is the energy of Pd(1 1 1).

3 Results and discussion

For the methanol adsorption on Pd(1 1 1) surface with and without electric field, two initial configurations with C-O bond axis perpendicular to the Pd(1 1 1) surface have been studied. For one, as shown in figure 1a, the methanol molecule adsorbed on the Pd(1 1 1) surface with initial hydroxyl close to the Pd(1 1 1); and for the other, methyl was near the Pd(1 1 1) surface as shown in figure 1b. The optimized adsorption configurations were shown in figure 2a and figure 2b, respectively. Methanol tilted a little bit with an angle of 87.8° formed by C-O

bond axis and Pt(111) surface when the initial methanol adsorbed through methyl mode. While it became 63.2° when the initial methanol adsorbed through hydroxyl configuration. The adsorption energy of methanol molecule through methyl is -39.38 kJ/mol, while it is -36.76 kJ/mol through hydroxyl, the gap between the two adsorption energy is only 2.62 kJ/mol. Thus it can be deemed that the methanol can adsorb either through methyl or hydroxyl on the Pd(1 1 1). When the Pd(111) surface is large enough, the two adsorption configurations of methanol may exist at the same time. Moreover, it can be found that all the bonds of methanol adsorbed on Pd(1 1 1) are almost similar with the free methanol molecule. The two optimized configurations were then used as the initial structure to study the effect of electric field on the Pd(1 1 1) surface.

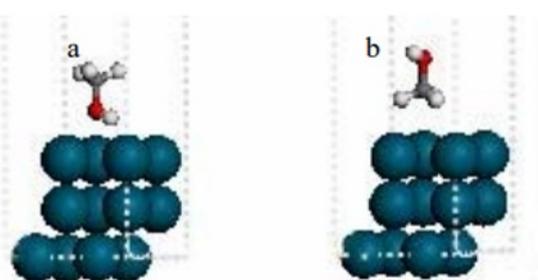


Fig. 1 The initial adsorption model of methanol
 (a) hydroxyl mode, (b) methyl mode
 Gray:C, Red: O, Blue Pd and White:H

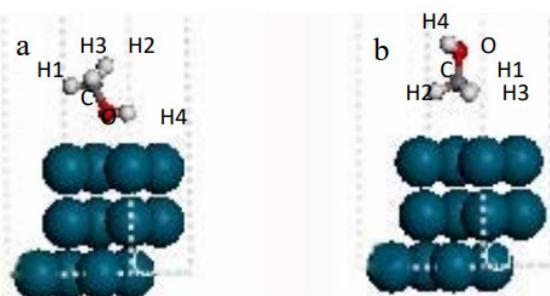


Fig. 2 The optimized adsorption of methanol without electric field
 (a) hydroxyl mode, (b) methyl mode

Table 1. Geometry of methanol adsorption on (2×2) Pd(1 1 1) surface in different electric field

	Methanol adsorption through methyl				Methanol adsorption through hydroxyl				
Elec/au	0.000	0.001	0.0025	0.005	Elec/au	0.000	0.001	0.0025	0.005
$\theta_{\text{surf-CO}}/^\circ$	87.8	87.9	54.9	1.9	$\theta_{\text{surf-CO}}/^\circ$	63.2	32.3	34.0	38.3
$d_{\text{Pd-C}}/\text{\AA}$	3.447	3.399	3.577	3.239	$d_{\text{Pd-O}}/\text{\AA}$	2.486	2.411	2.395	2.360
$d_{\text{surf-H1}}/\text{\AA}$	3.094	3.032	2.529	2.140	$d_{\text{surf-H4}}/\text{\AA}$	2.293	2.279	2.330	2.488
$d_{\text{surf-H2}}/\text{\AA}$	2.991	2.935	3.405	3.606					
$d_{\text{surf-H3}}/\text{\AA}$	3.051	3.001	2.681	3.678					

Elec represents the electric field, au is atomic units (equal to 5.14 V/nm), $\theta_{\text{surf-CO}}$ represents the angle between the Pd(1 1 1) surface and the C-O bond axis, d means various distances.

Table 1 shows the methanol adsorption on the Pd(1 1 1) surface both through methyl and hydroxyl in the electric field ranging from 0 to 0.005 au. As shown in table 1 and figure 3, it can be found that the initial C-O bond axis almost perpendicular to the Pd(1 1 1) surface became almost parallel to the metal surface with the increase of electric field intensity. For the adsorption of methanol through hydroxyl group in the electric field, the angle between the Pd(1 1 1) surface and the C-O bond

axis was reduced by $35 \pm 5^\circ$ when the minimized 0.001 au electric field was added to the system. However, as the electric field increases, the changes of adsorption configurations were not significant, and the $\theta_{\text{surf-CO}}$ were always within $35 \pm 5^\circ$. The H atoms in the hydroxyl group move away from the Pd(1 1 1) surface, the corresponding O atoms will be close to the Pd(1 1 1) surface, but the changes were not obvious.

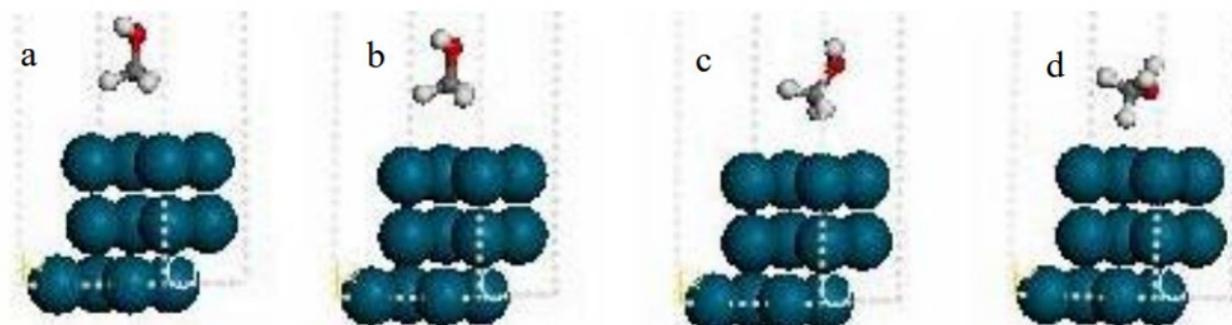


Fig. 3 Methanol adsorption on Pd(1 1 1) in (a) 0.000, (b) 0.0010, (c) 0.0025 and (d) 0.0050 au electric field.

The molecular configuration of methanol adsorbed through methyl was greatly affected by the electric field intensity. The distances between three H atoms and Pd(1 1 1) surfaces in methyl group were obviously different from each other. And the larger the electric field intensity, the smaller the angle between the C-O bond axis of methanol and the Pd(1 1 1) surface. When the electric field intensity is 0.001 au, the C-O bond of methanol molecule almost kept perpendicular to the Pd(1 1 1) surface, and the three hydrogen atoms on the methyl group are almost in the same plane; when the electric field intensity is 0.0025 au, the C-O bond axis deviates from the perpendicular direction of the surface about 35° , while the H1 and H3 atoms in the methyl group move forward to the Pd(1 1 1) surface and the H2 atoms goes far away from the Pd(1 1 1) surface; when the electric field intensity is 0.0050 au, the angle reduced to 1.9° , and the C-O bond is almost parallel to the Pd(1 1 1) surface. The H1 atom in the hydroxyl group became closer to the Pd(1 1 1) surface, H2 and H3 atoms in the methyl group goes farther away from the Pd(1 1 1) surface.

4 Conclusions

The electric field obviously affects the adsorption configuration of methanol under vacuum. In the absence of electric field, the methanol may adsorbed on the Pd(1 1 1) either through the methyl or the hydroxyl group, since the energy gap between the two configurations is just 2.62 kJ/mol. When an electric field was introduced to the system, for the methyl adsorption mode, the C-O bond axis will deviate from the perpendicular direction of the Pd(1 1 1) surface. The larger the electric field intensity, the smaller the angle between the C-O bond axis and the Pd(1 1 1) surface, and the C-O bond axis became almost parallel to the Pd(1 1 1) surface when the electric field intensity value is 0.0050 au. For the hydroxyl adsorption mode, $\theta_{\text{surf-CO}}$, the angle between the Pd(1 1 1) surface and the C-O bond axis remains $35 \pm 5^\circ$ in all the studied electric field intensity.

Acknowledgements

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