

# The anode oxidation reaction in fuel cell: A DFT study

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**Abstract.** Although fuel cell (FC) has been regarded as promising “green” power generator, the Pt-based catalysts in the FC hampered their further development for its high cost and scarcity. Direct methanol fuel cell (DMFC) as another kind of proton exchange membrane fuel cell (PEMFC) has been manifested that Pd also performs a certain activity for methanol oxidation reaction (MOR). To better know the mechanism of MOR, we present a DFT study on the first step reaction of MOR on the Pd(111). The results show that methanol prefers to physically adsorb on the Pd(111) through oxygen atom, while the dehydrogenated hydrogen atoms can adsorb either on face-centered cubic (FCC) or hexagonal close packed (HCP) sites. The intermediate products will form a much stronger interaction with the Pd(111) since they contain more unsaturated bonds. The energy barrier of O-H bond scission is most favourable, while the C-O bond is unfavourable in the first step of MOR.

## 1 Introduction

With the increasing severity of environmental pollution and global energy crisis, fuel cells as “green” energy conversion systems have attracted more and more attentions. [1, 2] FC can convert chemical energy directly into electric energy, and the products contain no pollution products. DMFC can also offer remarkably higher energy utilization efficiency but emits only CO<sub>2</sub>. In addition, methanol can be synthesized by decomposing biomass fuel, which has abundant sources and lower energy consumption. However, the sluggish methanol oxidation kinetics is still an important issue, since the MOR is a complex reaction containing 6 electrons transference.

A better understanding of the reaction mechanism of MOR is of great significance to improve the reaction kinetics. Experimentally, research on the mechanism of MOR on the surface of transition metals was mainly focused on the single crystal surface under ultra-high vacuum conditions. And modern surface instruments have been used to study the exact broken bonds during MOR. Levis [3] observed the presence of methyl group on Pd(111) surface with x-ray photoelectron spectroscopy (XPS). Guo [4] did not observe the broken C-O bond with isotope method. While Kruse [5] found both CH<sub>3</sub> and CH<sub>3</sub>O on the Pd(111) at the same time. Many scientists believe that CH<sub>x</sub>O (x=1-3) is produced only by O-H bond breaking during methanol decomposition on Pd surface. However, Chen [6] considered that the dissociation of methanol is not only the above two processes, but may be carried out

simultaneously or affected by the surface coverage. Theoretically, Hu [7] found that the O-H bond breaking was much easier. Though the study on the mechanism of MOR has attracted much attention, the exact broken bond in the first step of MOR is still controversial. Thus, the adsorption of methanol, co-adsorption of its intermediate products, and the reaction energy barrier of the first step in MOR have been studied in this paper.

## 2 Calculation model and method

The PW91 method based on the generalized gradient approximation is used to calculate the exchange correlation energy. And the transition state is searched with linear synchronous transit (LST) method. A 2×2 three-layer Pd(111) is chosen as our slab model, and a vacuum of 11.23 Å which is 5 times of Pd layer spacing is built to create a two-dimensional Pd(111) surface. The lower two layers are fixed at their optimized positions while the top atomic layer is thoroughly relaxed in all calculations. A Fermi surface smearing of 0.01 a.u. is utilized to speed up the convergence of k-point sampling. K point of the first Brillouin zone is set to 4×4×1. The adsorption energy is calculated according to the formula 1.

$$E_{\text{ads}} = E_{\text{complex}} - (E_{\text{Pd}} + E_{\text{A}}) \quad (1)$$

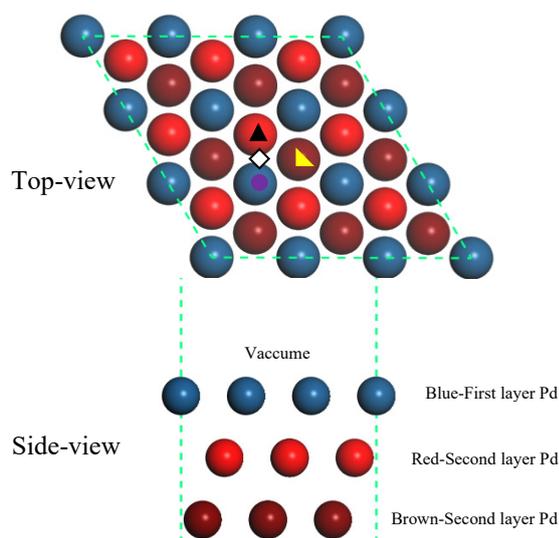
$E_{\text{ads}}$  is the adsorption energy,  $E_{\text{complex}}$  is the total energy of the system after species adsorption,  $E_{\text{Pd}}$  is the energy of clean Pd(111) surface,  $E_{\text{A}}$  is the energy of adsorbed species.

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### 3 Results and discussion

Adsorption is always the beginning step in every catalytic reaction. Herein, the adsorption of methanol and its intermediate products on Pd(111) are studied. And all the adsorptions at high symmetry sites on Pd(111) as shown in figure 1 are considered.

#### 3.1. Methanol adsorption



**Figure 1.** The high symmetry adsorption sites on Pd(111) (▲ HCP site, ▼ FCC site, ● Top site, ◇ bridge site)

**Table 1.** The adsorption structures of methanol on Pd(111)

Adsorption Site	$d_{O-H}$ (Å)	$d_{O-C}$ (Å)	$d_{O-Pd}$ (Å)	$d_{C-H}$ (Å)
Free	0.969	1.425	---	1.078;1.079;1.079
O-Top	0.958	1.415	2.63	1.078;1.084;1.083
O-FCC	0.961	1.406	3.32	1.079;1.074;1.080
O-HCP	0.960	1.405	3.31	1.075;1.078;1.079
Parallel → Top*	0.967	1.424	2.73	1.079;1.081;1.081
CH <sub>3</sub> -Top	0.956	1.411	---	1.078;1.085;1.086
CH <sub>3</sub> -FCC	0.956	1.402	---	1.079;1.088;1.088

\* The original parallel adsorption mode changed to Top mode without any energy barrier.

Figure 1 shows the high symmetry sites on the Pd(111), the methanol and related intermediates products adsorbed on the sites are calculated in this paper. The possible adsorption modes of methanol either through CH<sub>3</sub> or OH on the high symmetry sites of Pd(111) surface are calculated and the results are listed in table 1 and table 2. The bond length of O-H in free methanol is 0.969 Å, and all the adsorption OH bonds decrease a little bit. For the adsorption of methanol through the O

atom, it is 0.958 Å in the O-Top mode, while it becomes 0.961 Å for the O-FCC mode and 0.960 Å for the O-HCP mode. It gets the largest value of 0.967 Å when the original parallel mode turns to the O-top mode. For the adsorption of methanol through the CH<sub>3</sub>, it is 0.956 Å for the CH<sub>3</sub>-Top mode and CH<sub>3</sub>-FCC mode as well. The parallel adsorptive mode will change to a top adsorptive mode with OH close to the Pd(111), which means that the top adsorptive mode with oxygen closed to the surface is energetically favourable. The bond length of C-O in free methanol is 1.425 Å, and the C-O bond ranges from 1.405 Å to 1.415 Å in the O-mode adsorption. While it is 1.411 Å and 1.402 Å for CH<sub>3</sub>-Top mode and CH<sub>3</sub>-FCC mode, respectively. For the distances between O of methanol and Pd, it ranges from 2.63 Å to 3.32 Å except for the CH<sub>3</sub> mode. All the C-H bonds of the adsorbed methanol always keep the similar values with that in the free methanol, and the largest change can be obtained in the CH<sub>3</sub>-FCC mode.

**Table 2.** The adsorption energy ( $E_{ads}$ , kJ/mol) of methanol on Pd(111)

Adsorption Site	O-Top	O-FCC	O-HCP	C-Top	C-FCC
$E_{ads}$ (kJ/mol)	-38.20	-25.13	-25.04	-23.62	-25.43

The adsorption energy of methanol on Pd(111) is also calculated. As listed in Table 2, the adsorption energy of methanol with O-Top mode is -38.20 kJ/mol, which is energy most favourable. And it is -23.62 kJ/mol for the C-Top mode. The energy difference between each configuration is not very large, and the most favourable adsorption mode of methanol on Pd(111) is through O atom. Together with the structural properties listed in table 1, it can be found that three C-H bonds of the most favourable adsorptive methanol are 1.079 Å, 1.081 Å and 1.081 Å, respectively. A little elongation of C-H bond can be observed compared with that of free methanol molecule. While the O-H bond and C-O bond become about 0.01 Å shorter than the free methanol molecule. Compared with the original bonds in the free methanol molecule, all the distances between each atom almost keep its original value. This indicates that only physical adsorption occurs when methanol is adsorbed on Pd(111) surface. The weak interaction may lie in the d electrons of Pd and the lone pair electrons of O atom in methanol molecule.

#### 3.2 Hydrogen atom adsorption

H atom is the main product of methanol dissociation. The adsorption of H atom at four high symmetry positions on Pd(111) surface is calculated in this section, and the results are listed in table 3.

It can be found that H atom mainly adsorbs at HCP and FCC sites, and the H atom adsorbed at the bridge site will spontaneously move to the adjacent FCC sites during the optimization process. The adsorption energy of top H atom is -227.75 kJ/mol, and the Pd-H distance is 1.529 Å. It is about 40 kJ/mol lower than that at both

FCC and HCP sites. The average distance of Pd-H distance at the FCC site is 0.932 Å, which is 0.012 Å than that at HCP site. The covalent radii of hydrogen and Pd atom are 0.37 Å and 1.23 Å, respectively. However, it can be found that the Pd-H distances become even shorter than the covalent radii of Pd atoms. The significant shortened distance between H and Pd indicates that H and Pd have strong covalent interaction and form multiple hydrogen bonds, which should be the main reason for the energy reduction. Thus, the hydrogen atom is put on the FCC site when we perform the calculation of transition state search.

**Table 3.** The adsorption of H atom on Pd(111)

ads-site	Top	FCC*	HCP	FCC
$d_{\text{surf-H}}$ (Å)	1.529	0.934	0.944	0.932
$E_{\text{ads}}$ (kJ/mol)	-227.75	-267.53	-262.89	-267.12

\* The original site of H before optimization was bridge site.

### 3.3 Adsorption of other intermediate products

The intermediate products through the O-H, C-H and C-O bond scission are studied here, and the most stable configuration have been listed in table 4 and figure 2. For the adsorption of methoxy through O-H bond scission. The C-O bond axis is almost perpendicular to the Pd (111) surface with the O atom close to Pd(111). Compared with that in methanol, the oxygen in the methoxy has a larger electron density due to the lack of a hydrogen atom, which leads to a stronger interaction between methoxy and the d electrons of Pd. This is also the reason why the interaction energy of CH<sub>3</sub>O with Pd is larger at the triple vacancy.

**Table 4.** The most favourable adsorption site and adsorption energy of intermediate products on Pd(111)

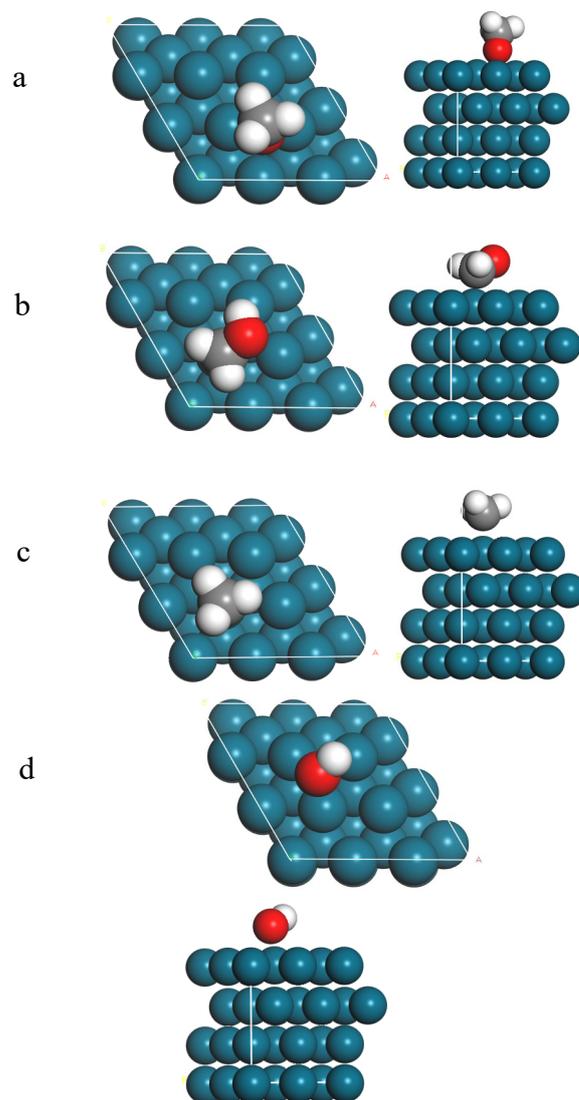
intermediate products	CH <sub>3</sub> O	CH <sub>2</sub> OH*	CH <sub>3</sub>	OH
Adsorption site	FCC	C-top and O-FCC	Top	Bridge
$E_{\text{ads}}$ (kJ/mol)	-157.00	-177.62	-179.61	-227.85

\* CH<sub>2</sub>OH adsorbs on Pd(111) through both C and O atoms.

For the adsorption of CH<sub>2</sub>OH through C-H bond scission. The adsorption of CH<sub>2</sub>OH on the Pd(111) with the C-O axis parallel to the Pd(111) surface. The adsorption energy is -177.62 kJ/mol, which is about 20 kJ/mol more stable than that of methoxy.

For the adsorption of CH<sub>3</sub> and OH through C-O bond scission. CH<sub>3</sub> prefers to adsorb on the top of Pd with an adsorption energy of -179.61 kJ/mol, and the distance

between C and Pd is 2.07 Å. OH prefers to adsorb on the bridge site of Pd(111), and the distance of O-Pd spacing is 2.15 Å.

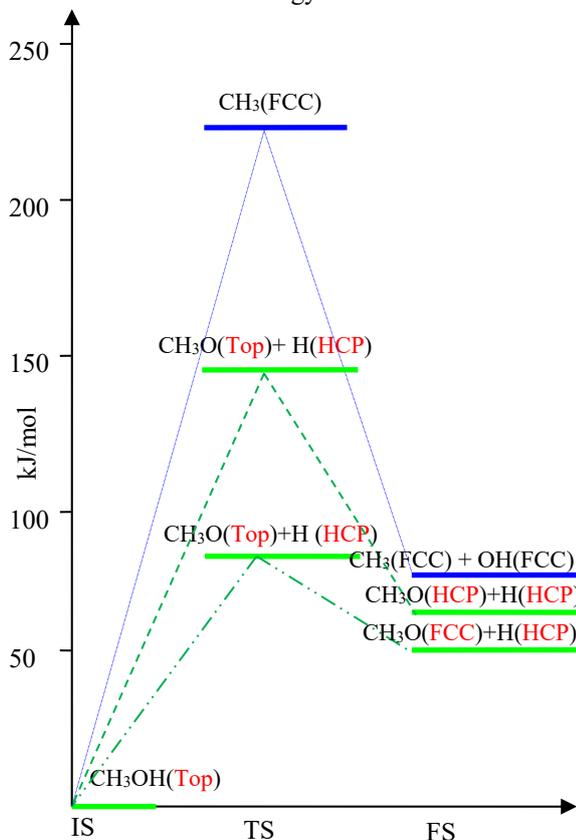


**Figure 2.** The most favourable adsorption structures of the intermediate products (a) CH<sub>3</sub>O, (b) CH<sub>2</sub>OH, (c) CH<sub>3</sub>, and (d) OH on Pd(111). (Red: Oxygen atom, Gray: Carbon atom, White: Hydrogen atom, Blue: Palladium atom. Left: top-view, Right: side-view)

### 3.4 Reaction energy barrier

The possible co-adsorptions of various intermediate products were optimized through putting the intermediates at their most favourable positions. Then we use the methanol adsorbed on Pd(111) as the initial state (IS), and optimized intermediate products co-adsorbed on Pd(111) as the products to perform a transition state (TS) search. The calculated reaction energy barrier is listed in figure 3. It can be found that the O-H bond scission will proceed easily while C-O bond scission is unfavourable, since the energy barrier of O-H bond scission is only 76.48 kJ/mol, while the energy barrier of C-O bond scission increases to 218.42 kJ/mol. The more the energy barrier, the more difficult

the reaction proceeds. Furthermore, different reaction paths can be found for the bond scission of O-H. For the final state (FS) of co-adsorption of CH<sub>3</sub>O at the FCC site and H at the HCP site, a transition state with CH<sub>3</sub>O at the Top site and H at the HCP site can be determined, and this route has the lowest energy barrier.



**Figure 3.** TS search for the dissociation of methanol in the first-step reaction

## 4 Conclusions

Methanol molecules only form weak physical adsorption on Pd(111) surface. The energy difference among each configurations is not very large, and the most favourable adsorption mode of methanol on Pd(111) is through O atom with an adsorption energy of -38.20kJ/mol. The H atom prefers to adsorbed at the FCC and HCP sites and the significant shortened distance between H and Pd indicates that H and Pd have strong covalent interaction and form multiple hydrogen bonds. The dissociative intermediate products of methanol usually form strong interaction with Pd(111) atoms because of the existence of unsaturated bonds. Compared with the C-O bond scission, the O-H bond broken on Pd(111) has a significantly smaller energy barrier, so it is considered that the first step breaking of methanol is mainly O-H bond breaking.

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