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First-principles Study of Adsorption and Dissociation of Methanol on the Pt(100) Surface

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Using first-principles calculations, we studied the interaction of methanol with the Pt(100) surface based on generalized gradient approximation. We found that top sites of Pt(100) surface are the favored adsorptive positions in energy, and methanol molecule interacts with the Pt surface through oxygen atoms. Moreover, we also explored the possible dissociation pathways of methanol on the Pt surface, and suggested that the products of dissociation can be controlled by the external manipulation.

Key words: Methanol, Pt(100) surface, Adsorption, Dissociation

I. INTRODUCTION

Organic molecules have been extensively studied, because of their potential applications in thermal and photo-catalytic oxidation [1–4]. Through the interaction with metal surfaces, these organic molecules show many interesting and amazing phenomena. Among these molecules, methanol is often adopted as a detector to investigate the intrinsic properties of metal surfaces [5–7]. In addition, methanol also shows the important role to evaluate the photo-catalytic activity of metal surfaces [8]. Therefore, the interaction between methanol and metal surfaces is of importance in understanding a number of relevant surface catalytic processes at the atomic scale [9–11]. A lot of efforts have been devoted to the study of methanol chemical adsorption on transition metal surfaces [12–16]. As revealed by the previous reports [17, 18], Pt, one of the most studied transition metal catalyst, has been found to be highly active catalyst for methanol molecule. Researchers have investigated the adsorption of methanol on Pt surfaces extensively by several experimental tools, such as EELS, STM, LEED and calorimetric measurements [19–21]. On the Pt(111) surface, Greeley *et al.* [22] and Desai *et al.* [23] have investigated adsorption of methanol by performing DFT calculations, and found the top sites are the preferred positions with an adsorption energies of 0.33 and 0.45 eV, respectively. Using the cluster model, Desai *et al.* found the adsorption energy is 0.65 eV [23]. Considering the edge effects from

the cluster model, the energy difference of adsorption is reasonable. Since methanol can also be readily converted to hydrogen, formaldehyde, dimethoxymethane and alkenes [24–26], methanol dissociation can proceed via three routes involving the breaking of O–H, C–O, and C–H bonds, respectively, depending on the catalyst. The special dissociative route is determined by the used catalyst and the C–H scission was theoretically proposed as the initial dissociation step on the Pt(111) [23].

Similar to Pt(111) surface, Pt(100) surface has also attracted many research interests. Although many works have demonstrated the significant difference from Pt(111) surface [27–29], the reported results about methanol adsorption on Pt(100) surface are still scarce. Kizhakevariam *et al.* investigated the reaction of methanol on clean and modified Pt(100) [30]. They found the reactivity of Pt(100) towards methanol depends on surface structure and the nature and amount of co-adsorbed reaction modifiers. They investigated the adsorption and reaction of CH₃OH with co-adsorbed O and CO in ultrahigh vacuum on the clean 1×1 surfaces of Pt(100), using the thermal desorption spectroscopy and high resolution electron energy loss spectroscopy. Methanol adsorbs molecularly on Pt(100) at 100 K and decomposes to adsorptive H and CO in the temperature range of 170–220 K. The vibrational spectra demonstrate the evidence for surface interactions involving both the hydroxyl (O–H···Pt) and methyl (C–H···Pt) hydrogen of molecular methanol. They also show that reaction with pre-adsorbed oxygen leads to a methoxy intermediate (CH₃O) and enhancement for oxygen coverage.

To the best of our knowledge, there is no detailed and systematic first-principles study on how methanol

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interacts with Pt(100) surface and how methanol dissociates on the surface. In order to reveal the difference of interactions between methanol and Pt surfaces, it is necessary to get the atomic understanding of these interactions. To address these issues, we have studied the adsorption of methanol at Pt(100) surfaces employing density functional theory.

In this work, we perform first-principles studies to investigate the energies, geometries, and the dissociation pathway of methanol on the Pt(100) surface. Since it has been found that methanol molecules can dissociate to form methyl and hydroxyl groups and then the dissociative adsorptions will take place on Pt surface, we have investigated the possible dissociative products of methanol on Pt(100) surface in our calculations, and the dissociative barrier is also calculated.

II. COMPUTATIONAL METHOD

Our calculations on methanol adsorption on the Pt(100) surface were performed using the VASP code [31]. The projector augmented wave potentials were employed to represent the interaction between ions and electrons [32]. The wave functions were expanded in the plane-wave basis up to a kinetic energy of 400 eV. Exchange correlation was described using the parametrization of Perdew, Burke, and Ernzerhof within the generalized gradient approximation (PBE-GGA) [33–36], which has been successfully applied to the calculations of similar problems. For the results presented here, a slab formed by five Pt layers was used. Chemisorbed species were placed on only one face of the slab. A 3×3 unit cell was considered for methanol adsorption, corresponding to a surface coverage of 1/9 ML when there was only one adsorbate per unit cell.

The slab is reproduced periodically in the perpendicular direction. The layers were separated by a 15 Å thick vacuum layer. Brillouin zone was carried out using the Monkhorst-Pack grid of $4 \times 4 \times 1$. During the optimizations, the upper-most three layers as well as the adsorbed molecule were allowed to relax until atom forces below 0.02 eV/Å. Total energies are extrapolated to zero temperature. The climbing-image nudged elastic band method (cNEB) was used to find the saddle points along the minimal energy pathway through the minimization of a set of four intermediate images with the force convergence criterion of 0.02 eV/Å [37]. The calculated PBE equilibrium lattice constant for the bulk is 4.00 Å, in agreement with the experimentally determined value of 3.92 Å [38].

III. RESULTS AND DISCUSSION

A. Methanol adsorption on the Pt(100) surface

We investigated the molecular adsorption of methanol (CH₃OH) on the Pt(100) surface. The

TABLE I Calculated and experimental structural parameters (bond length d and bond angle \angle) of CH₃OH molecule.

	Calculated	Experiment [39, 42]
$d_{C-O}/\text{Å}$	1.42	1.43
$d_{O-H}/\text{Å}$	0.96	0.95
$d_{C-H}/\text{Å}$	1.10	1.09
$\angle H-C-H/(\text{°})$	108.9	109.0
$\angle C-O-H/(\text{°})$	108.6	108.5

adsorption energies, E_{ads} , were calculated as:

$$E_{\text{ads}} = E_{\text{CH}_3\text{OH}} + E_{\text{Pt}} - E_{\text{CH}_3\text{OH}/\text{Pt}} \quad (1)$$

where $E_{\text{CH}_3\text{OH}}$ is the total energy of the free CH₃OH molecule in the gas phase, E_{Pt} is the total energy of the clean Pt(100) slab and $E_{\text{CH}_3\text{OH}/\text{Pt}}$ is the total energy of the CH₃OH/Pt system. Thus a positive E_{ads} corresponds to a stable CH₃OH/Pt system, suggesting the chemical interaction happened between CH₃OH and Pt slab. The energy of the isolated CH₃OH molecule was determined by calculating a single molecule in a cubic cell with a parameter of 15 Å. We made sure that the properties of the isolated molecule were accurately reproduced.

Before exploring the adsorption of methanol molecule, we firstly optimized the structure of isolated methanol molecule. As shown in Table I, our calculated results agree well with the experiments. As reported previously [39], the adsorption energies oscillate between the odd and even number of layers and converge slowly as the number of layers is increased. We have made the tests using the (2×2) unit cell slab model with different thicknesses. The layer number of Pt slabs has been changed from three to nine and it's found the difference of methanol adsorption energies is smaller than 0.04 eV when the number is larger than five, so we take the five-layer slab as our structure model.

To get ground state of adsorbed molecules on Pt(100) surface, we considered three symmetric adsorption sites, namely, top, hollow and bridge sites, which are schematically shown in Fig.1. In accordance with the results found in the previous work [22], we performed our calculations with CH₃OH adsorbed molecularly on Pt(100) via the O atom.

We observed that the relaxed configurations are close to the initial guesses. The calculated adsorption energies are 0.38, 0.19, and 0.30 eV (see Table II) for adsorption at the top, bridge and hollow sites, respectively, indicating the weak interaction between methanol and Pt slab. Besides, we also found the energy difference among different adsorptive configurations is small. Therefore, it is difficult to control the adsorptive configurations of methanol molecule under room or higher temperature.

However, in the experimental work by Kizhakevariam *et al.* [30], they didn't report the detailed parameters

TABLE II Adsorption energies E_{ads} and structural parameters obtained for methanol adsorbed at the three sites of Pt(100). Z is vertical distances of atom and Pt surface plane.

Adsorption sites	E_{ads}/eV	Bond length $d/\text{\AA}$			$Z/\text{\AA}$		$\angle\text{C-O-H}/(^{\circ})$
		C-H	C-O	O-H	C-Pt	O-Pt	
Top	0.38	1.10(2), 1.09(1)	1.43	0.98	3.62	2.30	110.9
Bridge	0.19	1.10(2), 1.09(1)	1.43	0.97	3.71	2.59	111.2
Hollow	0.30	1.10(2), 1.09(1)	1.42	0.98	3.69	2.35	111.8

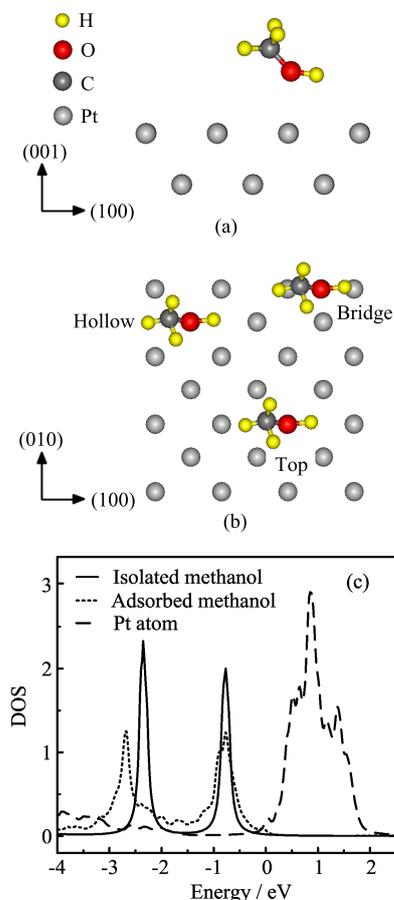


FIG. 1 (a) Side view of methanol adsorption structure on Pt(100) surface. (b) Top view of methanol adsorption structure on Pt(100) surface. For clarity, not all the surface is shown and only the first layer is included. (c) Density of states for methanol adsorbed on the top site.

for methanol adsorption on Pt(100). We stated our calculated optimized structural parameters in Table II. There is no significant difference in $\angle\text{H-C-H}$, C-H and C-O between gas-phase and adsorbed molecules. The $\angle\text{C-O-H}$ is increased from 108.6° in isolated methanol to 110.9° corresponding to methanol adsorbed on the top site. On the bridge and hollow sites, the values of this $\angle\text{C-O-H}$ are 111.2° and 110.8° , respectively. We have shown the vertical distances between oxygen and the Pt surface plane. The value for top site is 2.30 \AA , this distance is shorter than that of the

bridge (2.59 \AA) and hollow (2.35 \AA) sites. Desai *et al.* have performed similar calculations on Pt(111) surface [23], they found the values are 2.43 and 2.59 \AA for the top site and bridge site, respectively. It is believed that the adsorption of methanol appears to occur via oxygen atoms [40]. As shown in Fig.1(c), the projected density of states (PDOS) of isolated methanol shows two sharp peaks, which becomes shorter and wider for the adsorbed methanol. Moreover, we found the energy splitting between two peaks is widened, reflecting the chemical interaction between methanol and Pt atoms.

B. Methanol dissociation on the Pt(100) surface

Based on the above discussion, we find out the top site of Pt(100) surface is preferred site for the adsorption of CH₃OH to occur. To understand the properties and reactivity of methanol on the top site of Pt(100), the pathways of methanol dissociation are systematically examined. As already discussed, methanol dissociation can proceed via three routes involving the breaking of O-H, C-O, and C-H bonds, respectively. So we calculated the C-O, O-H, and C-H scissions and the pathways of intermediates dissociation on Pt(100).

The energy diagrams for methanol dissociation through C-O, O-H and C-H bond scission over the three clusters A, B, and C are shown in Fig.2. The stable geometry is obtained as the product of dissociating methanol over the surface, as shown in Fig.2. As shown in Fig.2, the pathway of C-O scission is initiated via TS1, producing methyl (CH₃) and hydroxyl group (OH) (FS1). The carbon in methyl exhibits sp^2 -like hybridization in TS1, while sp^3 -like hybridization in FS1. The C-O length elongates considerably from 1.43 \AA in IS to 2.21 \AA in TS1. This reaction is highly exothermic by 1.01 eV with an energy barrier of 1.55 eV , a relatively high value. The pathway of C-H scission starts with methanol dehydrogenation producing hydromethyl (CH₂OH). The C-H length elongates from 1.10 \AA in IS to 1.40 \AA in TS2. This reaction is exothermic by 0.64 eV with the lowest energy barrier of 1.09 eV . The pathway of O-H scission is initiated by the cleavage of the hydroxyl group via TS3, producing methoxide (CH₃O) (FS3). The hydrogen atom derived from the hydroxyl group is adsorbed on top Pt atom in TS3 and is transferred to O atom in FS3. The O-H length elongates considerably from 0.99 \AA in IS to 1.29 \AA in TS3.

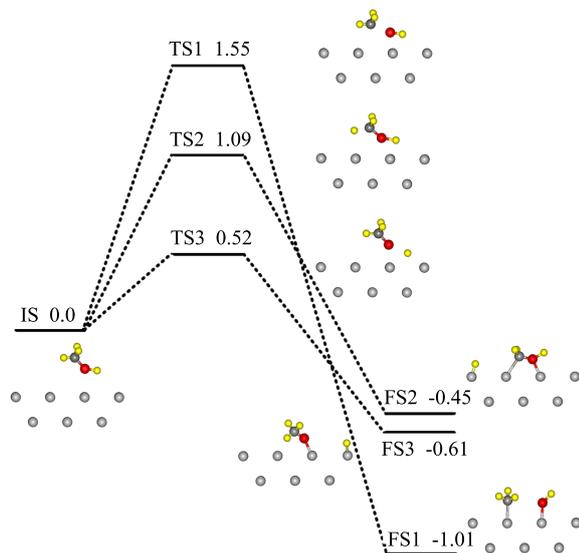


FIG. 2 Energy diagrams from methanol dissociation pathways. For TS_x and FS_x , $x=1, 2$ and 3 represent C–O, C–H, and O–H bond scission pathways, respectively. Energy unit is eV. IS represents the initial state (adsorbed methanol), TS_x and FS_x ($x=1, 2, 3$) represent the transition states and the final states in the reactions of bond scissions $x=1$, C–O; $x=2$, O–H; $x=3$, C–H, respectively.

This reaction is exothermic by 0.61 eV with an energy barrier of 0.52 eV.

Reaction energies and the activation barriers obtained here suggested that for the methanol dissociation on top Pt site, the three pathways are exothermic favorable. O–H scission to form the co-adsorbed CH_3O and hydrogen is kinetically preferred on top site. The activation barrier of the O–H scission is only 0.52 eV, much lower than the barriers of 1.09 eV for the C–H scission and 1.55 eV for C–O scission. Meanwhile, C–O scission is unfavorable although it produces stable product states.

C. Adsorption of intermediates from dissociation on the Pt(100) surface

During the dissociation, some fragments of methanol were produced, this section presents calculations of the chemisorption of CH_3O , CH_2OH , CH_2O , CH_3 , and CH_2 , which are all produced from the methanol dissociation. The adsorption energies of the intermediates and the C–O distances in the adsorbed and gas phase of these intermediates are listed in Table III.

CH_3O is adsorbed on Pt atom through its oxygen atom, which accounts for an adsorption energy of 2.89 eV. The C–O distance is 1.41 Å, elongated by 0.04 Å compared with that in gas phase. CH_2OH is formed via elimination of an H atom from the C center of methanol. CH_2OH is adsorbed with the adsorption energy of 2.27 eV. In CH_2OH , the C–O bond is elon-

TABLE III Adsorption energies E_{ads} and structural parameters of the intermediates from methanol dissociation at the three sites of Pt(100).

	E_{ads}/eV	$d_{C-O}/\text{Å}$	
		Gas phase	Adsorbed
CH_3O	2.89	1.37	1.41
CH_2OH	2.27	1.37	1.47
CH_2O	1.15	1.23	1.44
CH_3	1.62		

gated by about 0.10 Å compared with that in gas phase. It is noteworthy that the hybrid orbital of carbon is sp^3 in the adsorbed configuration, while sp^2 in the gas phase. Unlike CH_2OH , CH_2O is also adsorbed with lower adsorption energy of 1.15 eV. The C–O distance is 1.44 Å, elongated by up to 0.21 Å compared with 1.23 Å in the gas phase. It is presumed that the C–O bond is easy to break because of the large elongation of C–O bond length. CH_3 is adsorbed which accounts for the adsorption energy of 1.62 eV. The dehydrogenation of CH_3 may continue to form CH_2 .

Through comparing these intermediates adsorbed over the three clusters, it is found that their adsorption stability is in the order of $CH_3O > CH_2OH > CH_3 > CH_2O$. DFT calculations of various dehydrogenated intermediates (CH_3O , CH_2OH , CH_2O , and CHO) on Pd(111) suggested that the most favorable configurations are CH_3O and CH_2OH species [41]. Moreover, the Pd(111) surface also has an order of $CH_3O > CH_2OH > CH_3 > CH_2O$ for the adsorption stability. It is consistent with the result in our calculation. It indicates that Pt(100) is similar to other noble metal in the dissociative adsorption of methanol.

IV. CONCLUSION

We have performed plane-wave DFT calculations to determine the adsorption and dissociation of methanol on the Pt(100) surface. For the isolated methanol, d_{C-O} (1.43 Å), d_{O-H} (0.98 Å), and d_{C-H} (1.10 Å), $\angle H-C-H$ (108.8°) and $\angle C-O-H$ (108.7°) are in good agreements with experimental values. The results have shown that during the adsorption, d_{C-O} , d_{O-H} , and d_{C-H} , and $\angle H-C-H$ are not much affected. We also found $\angle C-O-H$ increased for all sites in the adsorption. Adsorption at the top site is the most stable for $CH_3OH/Pt(100)$ among the considered adsorption sites, adsorption hollow site is another stable site, with a higher energy of 0.08 eV. We compared the adsorption values with the methanol adsorption on Pt(111) surface, and we found it is the same that the methanol preferred binding to the top site via oxygen atoms on both surfaces with a similar adsorption energy value. We have systematically investigated the pathways for the methanol dissociation on the top site, in order to

understand the properties and reactivity of methanol on Pt(100). The O–H scission is found to be the most easily to happen, with only a 0.52 eV energy barrier, much lower than the barriers of 1.09 eV for the C–H scission and 1.55 eV for C–O scission. This is different from the dissociation behavior for methanol on Pt(111), since Desai *et al.* suggested the C–H scission was the most easily to happen on Pt(111) [23]. Calculations of the chemisorption of methoxide, hydroxylmethyl, formaldehyde, methyl and methylene, which are all produced from the methanol dissociation, were performed. We found their adsorption stability is in the order of $\text{CH}_3\text{O} > \text{CH}_2\text{OH} > \text{CH}_3 > \text{CH}_2\text{O}$.

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