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# A DFT study on the formation of $CH_3O$ on $Cu_2O(1\ 1\ 1)$ surface by $CH_3OH$ decomposition in the absence or presence of oxygen

## Zhang Riguang, Liu Hongyan, Ling Lixia, Li Zhong, Wang Baojun\*

Key Laboratory of Coal Science and Technology of Ministry of Education and Shanxi Province, Taiyuan University of Technology, No. 79 West Yingze, Taiyuan 030024, Shanxi, China

### ARTICLE INFO

Article history: Received 30 January 2010 Received in revised form 1 November 2010 Accepted 5 December 2010 Available online 13 December 2010

Keywords: Cu<sub>2</sub>O(111) Oxygen-precovered Methanol Methoxyl Density functional theory

### ABSTRACT

The formation mechanism of CH<sub>3</sub>O by the adsorption and decomposition of CH<sub>3</sub>OH on clean and oxygenprecovered Cu<sub>2</sub>O(111) surface has been investigated with density functional theory method together with the periodic slab models. Two possible formation pathways of CH<sub>3</sub>O by CH<sub>3</sub>OH decomposition on oxygen-precovered (O<sub>pre</sub>) Cu<sub>2</sub>O(111) surface were proposed and discussed. One is the O–H bondcleavage of CH<sub>3</sub>OH with H migration to O<sub>pre</sub> to form CH<sub>3</sub>O; the other is the C–O bond-scission of CH<sub>3</sub>OH with CH<sub>3</sub> migration to O<sub>pre</sub> leading to CH<sub>3</sub>O<sub>pre</sub>. The calculated results show that the O–H bond-breaking path has the lowest activation barrier 26.8 kJ mol<sup>-1</sup>, the presence of oxygen-precovered on Cu<sub>2</sub>O(111) surface exhibits a high surface reactivity toward the formation of CH<sub>3</sub>O by the O–H bond-cleavage of CH<sub>3</sub>OH, and reduce the activation barrier of O–H bond-cleavage. The C–O bond-breaking path was inhibited by dynamics, suggesting that the O atom of CH<sub>3</sub>O is not from the oxygen-precovered, but comes from the O of CH<sub>3</sub>OH. Meanwhile, the calculated results give a clear illustration about the formation mechanism of CH<sub>3</sub>O in the presence of oxygen and the role of oxygen at the microscopic level.

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### 1. Introduction

The oxidative carbonylation of methanol to DMC has received more attention than the other processes because of its abundant and inexpensive raw materials, as well as its environmentally friendly process [1-5]. Based on heterogeneous catalysts, researches about the oxidative carbonylation process, is mainly focused on copper [6], cobalt [7], and complexes of copper and palladium [8]. Copper heterogeneous catalysts feature low toxicity and low cost, and have shown high activity and selectivity to DMC when CuCl and CuCl<sub>2</sub> are used as the active components, but there are several problems such as the corrosion of the equipment and deactivation of the catalyst due to Cl- loss. In order to stabilize the Cu active centers, many kinds of base additives used as promoters or co-solvents (such as amines and pyridine), as well as immobilized copper salt catalysts on inorganic or organic solid materials have been investigated [1,9-12]. The deactivation and corrosion during the synthesis process are still the problems to restrict its commercial application because of the formation of HCl from the existing Cl<sup>-</sup> in catalysts. Therefore, it will be significant both theoretically and practically to avoid the deactivation and corrosion problems by developing a new technology for preparing catalysts with less or free Cl-.

Cu<sub>2</sub>O has been chosen as a free Cl<sup>-</sup> and ideal model system to investigate the catalytic mechanism for the oxidative carbonylation of methanol. King [13] has prepared the catalyst consisting of Cu<sub>2</sub>O and LZ-20 M zeolite to study the catalytic activity for the oxidative carbonylation of methanol. In our previous work [14], the free Cl<sup>-</sup> catalyst Cu<sub>2</sub>O/AC by dipping Cu(CH<sub>3</sub>COO)<sub>2</sub> onto activate carbon (AC) surface has been obtained. The experimental results show that the Cu<sub>2</sub>O/AC catalyst performs a good catalytic activity for the oxidative carbonylation of methanol, in which Cu<sub>2</sub>O has been postulated to be the catalytic active species.

Several studies about the mechanism and kinetics of DMC synthesis over Cu-exchanged zeolites have shown that CH<sub>3</sub>O adsorbed on the catalyst surface is an important intermediate in these reactions. Then, CO addition to adsorbed CH<sub>3</sub>O to form carbomethoxide species was proposed to be the rate-limiting step [5,13,15-17]. Based on evidence from in situ IR spectroscopy, King et al. [13,15] have proposed that CH<sub>3</sub>OH adsorbs on extra-framework Cu cations in Cu-Y and quickly react with oxygen to form CH<sub>3</sub>O. Anderson et al. [9,16,17] and Bell and co-workers [5] have shown that the CH<sub>3</sub>O adsorbed on catalyst can be easily formed by CH<sub>3</sub>OH decomposition in the presence of oxygen. And Chen et al. [18] have also found that the surface oxygen exhibits a high surface reactivity toward the formation of CH<sub>3</sub>O by CH<sub>3</sub>OH decomposition on CuCl(111) surface [19]. In other words, above researches also suggest that the presence of surface pre-covered oxygen plays a very important role for the formation of CH<sub>3</sub>O by CH<sub>3</sub>OH decomposition. But it is still unclear about the details of the catalytic mechanism of oxygen for the formation of CH<sub>3</sub>O. It is obvious that information about

<sup>\*</sup> Corresponding author. Tel.: +86 351 6018539. E-mail address: wangbaojun@tyut.edu.cn (W. Baojun).

<sup>0169-4332/\$ –</sup> see front matter 0 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.apsusc.2010.12.026

the interaction and reaction of small molecules, such as  $CH_3O$ , O and  $CH_3OH$ , adsorbed on  $Cu_2O$  surfaces is very important to understand the mechanism of these catalytic processes. Over the past decades, it has been demonstrated that theoretical techniques can serve as powerful tools for obtaining a fundamental understanding of chemistry reaction mechanisms [20]. Up to now, to the best of our knowledge, very few theoretical studies have been reported on the formation of  $CH_3O$  by  $CH_3OH$  decomposition on  $Cu_2O(111)$  surfaces in the presence of oxygen. Thus, it is very necessary and significant to explore the formation mechanism of  $CH_3O$  by  $CH_3OH$  decomposition on  $cu_2O(111)$  surface, and to understand the catalytic mechanism of oxygen.

In this study, particular attention is paid to the formation mechanism of CH<sub>3</sub>O by CH<sub>3</sub>OH decomposition on oxygen-precovered CuO<sub>2</sub>(111) surface. The density functional theory (DFT) together with periodic slab model was employed to investigate the adsorption geometries, adsorption energies and the relevant activation barriers for the formation of CH<sub>3</sub>O on oxygen-precovered Cu<sub>2</sub>O(111) surface. The following two questions by means of firstprinciples calculations wish to be solved at the microscopic level: (a) compared with clean Cu<sub>2</sub>O(111) surface, how does the presence of oxygen on Cu<sub>2</sub>O(111) surface affect the adsorption and decomposition behavior of CH<sub>3</sub>OH for the formation of CH<sub>3</sub>O; (b) Does the O atom in CH<sub>3</sub>O comes from either O atom of CH<sub>3</sub>OH or oxygen on Cu<sub>2</sub>O(111) surface.

#### 2. Model and computational methods

### 2.1. Surface models

The Cu<sub>2</sub>O(111) surface were modeled by using the supercell approach, where periodic boundary condition are applied to the central supercell so that it is reproduced periodically throughout space. The stoichiometric Cu<sub>2</sub>O(111) surface is non-polar, and includes four chemically distinguishable types of surface atoms which were denoted as Cu<sub>CUS</sub>, Cu<sub>CSA</sub>, O<sub>SUF</sub> and O<sub>SUB</sub>, as shown in Fig. 1. The Cu<sub>CUS</sub> is the surface copper that is singly-coordinate

Cu<sub>CUS</sub>\*

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unsaturated Cu<sup>+</sup> cations, which acts as a Lewis acid site. Cu<sub>CSA</sub> is doubly-coordinate saturated copper atom.  $O_{SUF}$  is the three foldcoordinate oxygen anions of the outer-most surface, which acts as a Lewis base site. And  $O_{SUB}$  is the four fold-coordinate oxygen anions of the subsurface. A [2 × 2] supercell with six atomic layers was used, as shown in Fig. 1, the vacuum space of 1.0 nm was inserted in the direction perpendicular to the surface, at such a distance there was little interaction between the neighboring layers.

### 2.2. Calculation methods

DFT has already been extensively used to study oxide surfaces and molecular adsorption on these surfaces. And this approach has been used in Chen's previous work on Cu<sub>2</sub>O [21,22], CuCl [23-25], Au [26,27] and Cu [28] surfaces. It is well known that molecular dissociation energies are very poorly reproduced with the local density approximation (LDA) commonly used in condensed-matter work, the generalized gradient approximation (GGA) is much more satisfactory, though it still does not give full chemical accuracy [29]. In our present work, DFT have been employed to perform for all calculations using GGA with the Becke-Lee-Yang-Parr (BLYP) exchange-correlation functional. In the computation, the inner electrons of copper atoms were kept frozen and replaced by an effective core potential (ECP), other atoms were treated with an all electron basis set. The double-numeric basis with polarization functions (DNP) is used for all atoms in the adsorbed and substrate systems. The *k*-point sampling scheme of Monkhorst–Pack grid of  $4 \times 4 \times 1$  and Methfessel–Paxton smearing of 0.005 hartree were employed. The converge criterion judged by the energy, force and displacement, respectively, were  $1 \times 10^{-5}$  Ha,  $2 \times 10^{-3}$  Ha/Å,  $5 \times 10^{-3}$  Å. All calculations were carried out with the Dmol<sup>3</sup> program package in Materials Studio 4.0 [30,31] on HP Proliant DL 380 G5 server system.

The adsorption energy is always regarded as a measure of the strength of adsorbate-substrate adsorption. The adsorption energies  $E_{ads}$  are defined as:  $E_{ads} = E_{substrate} + E_{adsorbate} - E_{adsorbate/substrate}$ , where  $E_{adsorbate/substrate}$  is the total energy of adsorbate-substrate



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Fig. 1. The slab model of  $Cu_2O(111)-2 \times 2$  (top view and side view).

### Table 1

Changes of atomic coordinate and bond length for clean Cu<sub>2</sub>O(111) surfaces<sup>a</sup>.

Site	$\Delta x$ (Å)	$\Delta y$ (Å)	$\Delta z$ (Å)	Bond	$\Delta L (\text{\AA})^{b}$
Cu <sub>CUS</sub> <sup>c</sup>	0.493	0.026	-0.359	Cu <sub>CUS</sub> –O <sub>SUB</sub>	0.184
Cu <sub>CSA</sub>	0.168	0.358	0.151	O <sub>SUF</sub> -Cu <sub>CSA</sub>	0.011
Cu <sub>SUF</sub>	0.400	0.229	0.194	O <sub>SUB</sub> -Cu <sub>CSA</sub>	0.054
Cu <sub>SUB</sub>	0.130	0.292	0.089	-	-

<sup>a</sup> The unit for atoms are in fractional coordination.

<sup>b</sup>  $\Delta L$ , the change of bond length.

<sup>c</sup> The subscripts for adsorption site in Table 1 can be seen in Fig. 1.

system in the equilibrium state, and  $E_{\rm substrate}$  and  $E_{\rm adsorbate}$  are the total energy of fixed substrate and free adsorbate alone, respectively. By this definition, positive value of adsorption energy denotes that adsorption is more stable than the corresponding substrate and free adsorbate.

### 2.3. Surface relaxation

The Cu<sub>2</sub>O(111)-2 × 2 surface relaxation was considered before calculating the adsorption systems. In this supercell, the lattice parameters are a = b = 12.076 Å, c = 13.698 Å. Vectors a, b and c amount to x, y and z axes directions, respectively, as shown in Fig. 1. The structural changes of various adsorption sites on Cu<sub>2</sub>O(111) surface are examined. Surface relaxation is found to be minimal, which suggests that surface relaxation is negligible. The changes are summarized in Table 1. Thus, the geometry of Cu<sub>2</sub>O(111) substrate can be kept fixed as it is in the bulk throughout the calculations, and the negligible relaxation is in accordance to the non-polar character of the surface [32]. Previous studies about NO [27], O<sub>2</sub> [33] and CO [34,35] adsorption and dissociation on Cu<sub>2</sub>O(111) substrate have also shown that surface relaxation was negligible and can been frozen in the calculation.

### 2.4. The size effect of surface on calculation

To investigate the necessary size for surface, the adsorption energy and optimized geometries of  $CH_3O$  adsorbed at  $Cu_{CUS}$  site with O-down were compared for different supercell. The  $Cu_{CUS}$  site was only considered according to the conclusion from the Section 3.2.2. Table 2 lists the equilibrium distances, adsorption energies and Mulliken charge.

As Table 2 presents, the adsorption energies have a relatively large change from the 1 to 1/4 ML coverages. However, the adsorption energies have few changes from 1/4 to 1/6 ML coverages, suggesting that whether we use  $[2 \times 2]$  or  $[2 \times 3]$  supercell, the same result is obtained. Hence, taking consideration into calculation efficiency, a  $[2 \times 2]$  supercell was employed in our study.

### 3. Results and discussion

# 3.1. The proposed mechanism for the formation of CH<sub>3</sub>O by CH<sub>3</sub>OH decomposition

The formation of CH<sub>3</sub>O by CH<sub>3</sub>OH decomposition begins with the adsorption of CH<sub>3</sub>OH from the gas phase onto Cu<sub>2</sub>O(111) surface. The adsorbed CH<sub>3</sub>OH can then decompose via a series of sequential steps to produce various intermediates [19]. The first decomposition step involves the activation of the C–H, O–H and C–O bonds of CH<sub>3</sub>OH to initiate the catalytic cycle. As for the C–H bond activation and scission, the resulting intermediates are CH<sub>2</sub>OH and H, so the C–H bond activation is not examined in this paper.

It is proposed that the possible reaction mechanisms for the formation of  $CH_3O$  on  $Cu_2O(111)$  surface by  $CH_3OH$  decomposition

$$CH_3O-H + * \rightarrow CH_3O + H$$
 Path 1

$$CH_3O-H + O_{pre} + * \rightarrow CH_3O + HO_{pre}$$
 Path 2

$$CH_3-OH + O_{pre} + * \rightarrow CH_3O_{pre} + HO$$
 Path 3

**Scheme 1.** The proposed mechanism for the formation of CH<sub>3</sub>O by CH<sub>3</sub>OH decomposition.

in the absence or presence of oxygen and it can be summarized as Scheme 1 describes (an asterisk is used to stand for an active site): Path 1 is the formation pathway of CH<sub>3</sub>O by the O–H bond-cleavage of CH<sub>3</sub>OH in the absence of oxygen on clean Cu<sub>2</sub>O(111) surface, the resulting intermediates are CH<sub>3</sub>O and H; Path 2 is the formation pathway of CH<sub>3</sub>O on Cu<sub>2</sub>O(111) surface by the O–H bond-cleavage of CH<sub>3</sub>OH in the presence of oxygen (O<sub>pre</sub>), the resulting intermediates of O–H scission with H migration to O<sub>pre</sub> are CH<sub>3</sub>O and HO<sub>pre</sub>; Path 3 is the formation pathway of CH<sub>3</sub>O on Cu<sub>2</sub>O(111) surface by the C–O cleavage of CH<sub>3</sub>OH in the presence of O<sub>pre</sub>, the resulting intermediates of C–O cleavage of CH<sub>3</sub>OH in the presence of O<sub>pre</sub>, the resulting intermediates of C–O scission with CH<sub>3</sub> migration to O<sub>pre</sub> are CH<sub>3</sub>O<sub>pre</sub> and HO.

# 3.2. Structures and energies of adsorbed intermediates on $Cu_2O(111)$ surface

### 3.2.1. CH<sub>3</sub>OH/Cu<sub>2</sub>O(111)

Table 3 presents the values of the equilibrium distances, adsorption energies and Mulliken charges for CH<sub>3</sub>OH adsorbed on the four different adsorption sites of clean Cu<sub>2</sub>O(111) surface. The adsorption energy of CH<sub>3</sub>OH adsorbed at Cu<sub>CUS</sub> site is found equal to 89.3 kJ mol<sup>-1</sup>, which is a chemisorption ( $E_{ads} > 40$  kJ mol<sup>-1</sup>). That is to say, Cu<sub>CUS</sub> site is the most energetically favorable. Fig. 2(a) presents the optimal structure of CH<sub>3</sub>OH molecule adsorbed on Cu<sub>CUS</sub> site of Cu<sub>2</sub>O(111) surface. For the other adsorption sites (except for Cu<sub>CUS</sub>), the distances of C–H, O–H, C–O bond and the angle of C–O–H are close to those of the gas phase CH<sub>3</sub>OH molecule (shown in Table 3), and the rather long  $d_{(O-X)}$  bond length (the range from 2.686 to 3.523 Å) in the optimized structure shows that the interaction of CH<sub>3</sub>OH with surface is very weak.

The Mulliken charges of CH<sub>3</sub>OH indicates that the adsorption of CH<sub>3</sub>OH appears to occur via a donation of a lone pair of electrons from the oxygen to Cu<sub>2</sub>O(111) surface. The more electrons CH<sub>3</sub>OH donate to Cu<sub>2</sub>O(111) surface, the stronger the interactions occur between them. As Table 3 presents, the charges of CH<sub>3</sub>OH adsorbed at Cu<sub>CUS</sub> site are more than that in other adsorption sites. Hence the values of Mulliken charge and adsorption energy indicate that the Cu<sub>CUS</sub> site is the most advantageous site for CH<sub>3</sub>OH adsorbed on Cu<sub>2</sub>O(111) surface.

### 3.2.2. CH<sub>3</sub>O/Cu<sub>2</sub>O(111)

During a full geometry optimization, the CH<sub>3</sub>O that are bound to Cu<sub>CSA</sub>, O<sub>SUF</sub> and O<sub>SUB</sub> on Cu<sub>2</sub>O(111) surface are found to readily migrate to the Cu<sub>CUS</sub> site. The Cu<sub>CUS</sub>-bound CH<sub>3</sub>O interacts with the surface through oxygen atom (Fig. 2(b)) and has an adsorp-

Table 2

The effect of the supercell size in the surface model on the adsorbed configuration, adsorption energies and Mulliken charges for CH<sub>3</sub>O adsorbed at Cu<sub>CUS</sub> site of Cu<sub>2</sub>O(111) surface.

Coverage <sup>a</sup> (ML)	<i>d</i> <sub>(C-O)</sub> (Å)	<i>d</i> <sub>(Cu-O)</sub> (Å)	∠COCu (°) <sup>b</sup>	$q_{(\mathrm{methoxyl})}^{\mathrm{c}}$	$E_{\rm ads}$ (kJ mol <sup>-1</sup> )
1	1.424	1.819	128.017	-0.204	215.0
1/2	1.412	1.820	127.973	-0.224	217.6
1/4	1.423	1.827	125.065	-0.244	224.9
1/6	1.420	1.824	125.279	-0.249	225.3

<sup>a</sup> ML, monolayer.

<sup>b</sup> The angle is defined as the angle between C–O axis and the binding surface Cu atom.

<sup>c</sup> The sum charge of all atoms in CH<sub>3</sub>O.

#### Table 3

The equilibrium distances, adsorption energies and Mulliken charges for CH<sub>3</sub>OH adsorbed at different adsorption sites of Cu<sub>2</sub>O(111) surface.

Site	$d_{\rm (C-H)}$ (Å)	$d_{(\mathrm{C-O})}$ (Å)	$d_{(O-H)}$ (Å)	∠COH (°)	$d_{(\mathrm{O}-\mathrm{X})}$ (Å) <sup>a</sup>	$E_{\rm ads}$ (kJ mol <sup>-1</sup> )	$q_{(\mathrm{methanol})}$
Cu <sub>CUS</sub>	1.095	1.470	0.974	110.9	2.006	89.3	0.203
Cu <sub>CSA</sub>	1.095	1.447	0.977	110.5	2.686	24.4	0.023
O <sub>SUF</sub>	1.096	1.440	0.982	109.7	2.819	31.6	-0.011
O <sub>SUB</sub>	1.092	1.450	0.976	109.7	3.523	22.5	0.022
Gas phase <sup>b</sup>	1.094	1.425	0.945	109.0	-	-	0.000
Gas phase <sup>c</sup>	1.094	1.440	0.972	107.8	-	-	0.000

<sup>a</sup>  $d_{(O-X)}$ , the distance between O atom of CH<sub>3</sub>OH and adsorption site atom.

<sup>b</sup> Experimental values are taken from Ref. [19].

<sup>c</sup> The calculated value for free CH<sub>3</sub>OH molecule.



**Fig. 2.** Optimized structure of methanol and intermediates adsorbed on Cu<sub>2</sub>O(111) surface. Orange black balls represent Cu atoms, red light balls represent O atoms, grey black balls represent C atoms and white light balls represent H atoms throughout this paper. (For interpretation of the references to color in this sentence, the reader is referred to the web version of the article)

tion energy of 224.9 kJ mol<sup>-1</sup>, which indicates a strong energetic preference for the  $Cu_{CUS}$  site over other adsorption sites. The optimized structure parameters were shown in Table 2; CH<sub>3</sub>O adsorbed at  $Cu_{CUS}$  site is the most advantageous adsorption model with the C–O–Cu angle of 125.1°.

### 3.2.3. 0/Cu<sub>2</sub>O(111)

For the adsorption of atomic oxygen, only singlet states are calculated in our studies. The strengths of atomic O adsorption at four distinct adsorption sites of the Cu<sub>2</sub>O(111) surface are in the following order: O<sub>pre</sub>–Cu<sub>CSA</sub> > O<sub>pre</sub>–Cu<sub>CUS</sub> > O<sub>pre</sub>–O<sub>SUB</sub> > O<sub>pre</sub>–O<sub>SUF</sub>. In the case of O adsorbed at Cu<sub>CSA</sub> site, initially the atomic oxygen lies above the Cu<sub>CSA</sub> site, the configuration was then optimized but the O<sub>pre</sub> bounds to three Cu atoms, i.e., one Cu<sub>CUS</sub> and two Cu<sub>CSA</sub> sites (see Fig. 2(c)), which reflects the important contribution from the nearby cations. The calculated results indicate that the Cu<sub>CSA</sub> site is more favorable than other adsorption sites, and the favorable adsorption model has an adsorption energy of 337.5 kJ mol<sup>-1</sup>. This was in agreement with Chen's previous work [33]. Therefore, the model of the oxygen atom bounding to three Cu atoms on Cu<sub>2</sub>O(111) surface is chosen as the oxygen-precovered Cu<sub>2</sub>O(111) surface.

### 3.2.4. OH/Cu<sub>2</sub>O(111)

Two molecular orientations, O-down and H-down, over four adsorption sites of the Cu<sub>2</sub>O(111) surface are considered. The O–H axis is perpendicular to the surface in all the optimized models. It is interesting to find that all the H-down models are converted to Cu<sub>CUS</sub>–OH model after optimization. And for the O-down molecular orientation, the adsorption models of Cu<sub>CSA</sub>, O<sub>SUF</sub> and O<sub>SUB</sub> site are shown to migrate to the Cu<sub>CUS</sub> site after optimization. Above calculation results show that the Cu<sub>CUS</sub> site is the most stable site for OH adsorption with an adsorption energy of 297.9 kJ mol<sup>-1</sup>. As shown in Fig. 2(d), the optimized distances of O–H and Cu–O are 0.974 and 1.816 Å, respectively. And the angle of H–O–Cu is 111.1°.

### 3.2.5. H/Cu<sub>2</sub>O(111)

For the adsorption of atomic hydrogen, the adsorption model of  $O_{SUB}$  site is found to migrate to the  $Cu_{CUS}$  site after optimization. The adsorption energies in the following order,  $H-Cu_{CUS} > H-O_{SUF} > H-Cu_{CSA}$ . The  $Cu_{CUS}$  site is the most stable site with an adsorption energy of 238.2 kJ mol<sup>-1</sup>. The optimized distance of H–Cu is 1.486 Å, and the angle of H–O–Cu is 180.0° (see Fig. 2(e)).

### 3.3. Reaction mechanism

According to above adsorption energies, the preferential adsorption site for each species involved in the formation of CH<sub>3</sub>O by CH<sub>3</sub>OH decomposition are obtained, it is evidently found that radical intermediates have a much stronger interaction with the surface than molecules. The detailed reaction mechanisms are explored by activation barrier calculations. To determine accurate activation barriers of CH<sub>3</sub>O formation by CH<sub>3</sub>OH decomposition, the transition states are searched by means of complete LST/QST for reactions [36], starting from reactants and products, the LST (Linear Synchronous Transit) method performs a single interpolation to a maximum energy, and the QST (Quadratic Synchronous Transit) method alternates searches for an energy maximum with constrained minimizations in order to refine the transition state to a high degree. This method has been applied to study the adsorption and dissociation of NO dimmer [29] and O<sub>2</sub> [33] on clean Cu<sub>2</sub>O(111) surface and other adsorption reactions occurred on metal surfaces [18]. To understand the formation mechanism of CH<sub>3</sub>O, what is to be investigated first is the O-H bond cleavage of CH<sub>3</sub>OH on clean  $Cu_2O(111)$  surface.

3.3.1. The formation of  $CH_3O$  by  $CH_3OH$  decomposition on clean  $Cu_2O(1\,1\,1)$  surface

The formation of CH<sub>3</sub>O by the O–H bond cleavage of CH<sub>3</sub>OH on clean Cu<sub>2</sub>O(111) surface is written as Path 1 in Scheme 1. The resulting intermediates are CH<sub>3</sub>O and H. It has been pointed out that the CH<sub>3</sub>O and H placed above surface Cu<sub>CUS</sub> sites is the most stable configuration. Hence, the most stable CH<sub>3</sub>OH configuration over Cu<sub>CUS</sub> site is chosen to be the initial state (R) (see Fig. 2(a)), and the final state consists of the coadsorption of CH<sub>3</sub>O and H on the closest Cu<sub>CUS</sub> sites, shown in Fig. 3 (P). The transition state structure is displayed in Fig. 3 (TS).

In the TS structure, CH<sub>3</sub>O still bind with Cu<sub>CUS</sub> through oxygen atom, the C–O and Cu–O bond length is 1.475 and 1.975 Å, respectively. However, the O–H bond is broken, the O–H distance is 1.922 Å. And the distance from hydrogen atom to target Cu<sub>CUS</sub> site is 5.005 Å. In the coadsorption configuration P, the C–O, Cu–O and O–H bond length is 1.423, 1.824 and 1.484 Å, respectively. The activation barrier for this reaction is 94.6 kJ mol<sup>-1</sup>, and the reaction is found to be slightly exothermic by 4.5 kJ mol<sup>-1</sup>.

# 3.3.2. The formation of $CH_3O$ by $CH_3OH$ decomposition on oxygen-precovered $Cu_2O(111)$ surface

3.3.2.1. The O–H bond cleavage of CH<sub>3</sub>OH. The formation of CH<sub>3</sub>O by the O–H bond cleavage of CH<sub>3</sub>OH on oxygen-precovered Cu<sub>2</sub>O(111) surface is written as Path 2 in Scheme 1. The coad-sorption configuration of CH<sub>3</sub>OH adsorbed on oxygen-precovered Cu<sub>2</sub>O(111) surface is shown in Fig. 4 (R1), which is chosen to be the initial state. In this coadsorption configuration, the O–H bond is more elongated to 0.983 Å from that in the case of molecular CH<sub>3</sub>OH (0.972 Å), but that of CH<sub>3</sub>OH adsorbed on clean Cu<sub>2</sub>O(111) surface is elongated to 0.974 Å, which means that the O–H bond is broken much more easily in the presence of oxygen-precovered surface. The main contribution to the O–H bond activation in the coadsorption configuration may be from the strong induced effect of O<sub>pre</sub> on the adjacent CH<sub>3</sub>OH adsorbed.

As the resulting intermediates of O–H bond-breaking are the coadsorption  $CH_3O$  and  $HO_{pre}$ , and the  $CH_3O$  and HO placed above  $Cu_{CUS}$  sites is the most stable configuration. Hence,  $CH_3O$  and  $HO_{pre}$  on the adjacent  $Cu_{CUS}$  sites are chosen as the final state, as shown



Fig. 3. Optimized structure of the transition states and the products for the O-H scission of CH<sub>3</sub>OH adsorbed on clean Cu<sub>2</sub>O(111) surface.



Fig. 4. Optimized structure of CH<sub>3</sub>OH, intermediates and transition states adsorbed on oxygen-precovered Cu<sub>2</sub>O(111) surface by the O-H bond cleavage.



Fig. 5. Optimized structure of the intermediates and transition states adsorbed on oxygen-precovered Cu<sub>2</sub>O(111) surface by the C–O bond cleavage.

in Fig. 4 (P1). The transition state search is performed for the reaction from R1 to P1, one transition states and one intermediate are located, and the corresponding structures are displayed in Fig. 4 (TS1 and IM1).

Starting from R1, as the O–H bond of CH<sub>3</sub>OH dissociates, the departing hydrogen atom begins to coordinate with a surface O<sub>pre</sub> to form CH<sub>3</sub>O and HO<sub>pre</sub>. After careful search for the transition state of R1  $\rightarrow$  IM1, it is discovered to be a non-potential-energy-barrier reaction. IM1 is stabilized by 22.5 kJ mol<sup>-1</sup> in energy compared to R1. In IM1, the CH<sub>3</sub>O binds on the Cu<sub>CUS</sub>–Cu<sub>CSA</sub> bridge site through oxygen atom, the C–O, O–Cu<sub>CUS</sub> and O–Cu<sub>CSA</sub> length is 1.434, 2.038 and 2.109 Å, respectively. The HO<sub>pre</sub> also binds on adjacent Cu<sub>CUS</sub>–Cu<sub>CSA</sub> bridge site through O<sub>pre</sub> atom, and the H–O<sub>pre</sub>, O–Cu<sub>CUS</sub> and O–Cu<sub>CSA</sub> distance is 0.976, 2.001 and 2.094 Å, respectively. Above calculated results show that the O–H bond-breaking path on oxygen-precovered Cu<sub>2</sub>O(111) surface is much easier to occur.

Then, HOpre in IM1 migration to adjacent Cu<sub>CUS</sub> site leads to the formation of product P1 via a transition state TS1, TS1 is 26.8 kJ mol<sup>-1</sup> higher in energy than R1. Therefore, the rate-controlled step of the total reaction  $R1 \rightarrow P1$  is the elementary reaction  $IM1 \rightarrow P1$ , the activation barrier of total reaction is 26.8 kJ mol<sup>-1</sup>, and the reaction is found to be exothermic by  $32.7 \text{ kJ} \text{ mol}^{-1}$ . Obviously, the calculated activation barrier on oxygen-precovered Cu<sub>2</sub>O(111) surface is considerably smaller than that on clean  $Cu_2O(111)$  surface, the difference between two different surfaces is 67.8 kJ mol<sup>-1</sup>. So the O-H bond cleavage of  $CH_3OH$  on clean  $Cu_2O(111)$  surface cannot compete with that on oxygen-precovered  $Cu_2O(111)$  surface. Above calculated results answer the first question proposed in Section 1, compared with clean  $Cu_2O(111)$  surface, the presence of  $O_{pre}$  on  $Cu_2O(111)$ surface obviously improve the catalytic activity of Cu<sub>2</sub>O for the formation of CH<sub>3</sub>O by CH<sub>3</sub>OH decomposition, and reduce the activation barrier of O-H bond cleavage in CH<sub>3</sub>OH, and also make the O-H bond cleavage more easier to form CH<sub>3</sub>O. The calculated results are in accordance with Bell et al.'s experimental results [5], the formation of CH<sub>3</sub>O on Cu-Y in the presence of oxygen occur with an apparent first-order rate coefficient, namely, methanol adsorbs on extra-framework Cu cations reacts rapidly with oxygen to form methoxide groups. And these findings are also in agreement with the experimental studies of King et al. [13,15].

3.3.2.2. The C-O bond cleavage of CH<sub>3</sub>OH. Following Scheme 1, besides the O-H bond cleavage, the C-O bond scission with CH<sub>3</sub> migration to O<sub>pre</sub> atom can also lead to CH<sub>3</sub>O<sub>pre</sub>, in which O comes from oxygen-precovered, as described in Path 3. The alternative coadsorption configuration of CH<sub>3</sub>OH adsorbed on oxygen-precovered  $Cu_2O(111)$  surface is shown in Fig. 5 (R2), in this configuration, the length of O-H bond is 0.973 Å, however, the length of C-O bond is less elongated to 1.448 Å from 1.440 Å in CH<sub>3</sub>OH, which is shorter than that (1.470 Å) of CH<sub>3</sub>OH adsorbed on clean  $Cu_2O(111)$  surface. The bond length indicates that the Opre little affect the C-O bond activation, so the C-O bond is broken much less. It is an indication that the higher activation barrier will be needed for the C-O bond cleavage. At the same time, the adsorption energy of coadsorption configuration (353.7 kJ mol<sup>-1</sup>) is lower than that of R1 (366.6 kJ mol $^{-1}$ ), but is still larger than the single adsorption energy of O atom or  $CH_3OH$ . Fig. 5 (R2) and (P2) are chosen as the initial and final states, respectively. As shown in Fig. 5, two transition states (TS2, TS3) and one intermediate (IM2) are obtained by the transition state search.

Starting from R2, R2 proceeds through a transition state TS2 of C-O bond cleavage and CH3 migration towards Opre, subsequently, the departing CH3 begins to coordinate with Opre and leaving hydroxyl to form intermediate IM2, which is similar with IM1 in structure. In the TS2 structure, the methyl and hydroxyl is inclined to keep away from the surface. The C-O bond is broken because the length of C-O bond is 2.491 Å, and the C-O<sub>pre</sub> bond length is 2.438 Å. TS2 was found to be 318.1 kJ mol<sup>-1</sup> higher in energy than R2. In IM2, the HO still binds on adjacent Cu<sub>CUS</sub>-Cu<sub>CSA</sub> bridge site through O atom, and the H-O, O-Cu<sub>CUS</sub> and O-Cu<sub>CSA</sub> distance is 0.976, 2.007 and 2.086 Å, respectively. The CH<sub>3</sub>O<sub>pre</sub> also binds on the Cu<sub>CUS</sub>-Cu<sub>CSA</sub> bridge site through O<sub>pre</sub> atom, the corresponding C-Opre, O-Cu<sub>CUS</sub> and O-Cu<sub>CSA</sub> length is 1.433, 2.027 and 2.119 Å, respectively. The energy barrier for this elementary reaction is 318.1 kJ mol<sup>-1</sup> and the reaction is found to be endothermic by 59.4 kJ mol<sup>-1</sup>.

As  $Cu_{CUS}$  site is the preferred adsorption site for  $CH_3O_{pre}$  and OH, so the  $CH_3O_{pre}$  and OH binding on bridge site in IM2 are not



Fig. 6. Reaction energy diagram for the formation of  $CH_3O$  by  $CH_3OH$  over  $Cu_2O(1\,1\,1)$  surface in the presence or absence of oxygen.

stable, IM2 can easily convert to P3 via another transition state TS3, in which the  $CH_3O_{pre}$  and OH placed over the adjacent  $Cu_{CUS}$  sites. In the TS3 structure,  $CH_3O_{pre}$  adsorbs at  $Cu_{CSA}$  site, the length of the C– $O_{pre}$  and  $Cu_{CSA}$ – $O_{pre}$  bond is 1.383 and 2.146 Å, respectively. OH adsorbs aslant at  $Cu_{CUS}$  site, the length of the H–O and O– $Cu_{CUS}$  bond is 0.976 and 1.941 Å, respectively. The angle of H–O– $Cu_{CUS}$  is 114.5°. TS3 is predicted to be 79.0 kJ mol<sup>-1</sup> higher in energy than IM2, and the reaction is highly exothermic with an energy of 127.2 kJ mol<sup>-1</sup>. Thus, the highest activation barrier along the C–O bond cleavage pathway occurs at TS2. The C–O bond cleavage is the rate-controlled step for the formation of  $CH_3O$ , and the corresponding activation barrier of total reaction is 318.1 kJ mol<sup>-1</sup>.

The energy dates of the possible elementary steps for the formation of CH<sub>3</sub>O by CH<sub>3</sub>OH decomposition on Cu<sub>2</sub>O(111) surface in the absence and presence of oxygen are listed in Fig. 6. As shown in Fig. 6, the activation barriers ( $E_a$ ) for the formation of CH<sub>3</sub>O by the O–H and C–O bond-breaking of CH<sub>3</sub>OH on Cu<sub>2</sub>O(111) surface in the presence of oxygen are found to be 26.8 and 318.1 kJ mol<sup>-1</sup>, respectively. The activation barrier for the O–H bond cleavage of CH<sub>3</sub>OH ( $E_a$  = 26.8 kJ mol<sup>-1</sup>) is found to be the lowest. So the most favorable pathway should be the O–H bond-breaking reaction, which is in line with our expectation. Above calculated results answer the second question proposed in Section 1, for the formation of CH<sub>3</sub>O in the presence of oxygen, the O atom in CH<sub>3</sub>O comes from the O of CH<sub>3</sub>OH, not from the oxygen-precovered.

Although experimental evidences could be obtained by isotope labeling, it is a pity that no experimental results are available for comparison with our calculated results. We expect some experiments should be performed to determine the interlayer sites and oxygen position for confirmation of our calculation in our future work.

### 4. Conclusions

A detailed density functional study with periodical slab calculations was performed to examine the formation mechanism of CH<sub>3</sub>O by the adsorption and decomposition of CH<sub>3</sub>OH on clean and oxygen-precovered Cu<sub>2</sub>O(111) surfaces at the microscopic level. The calculated results show that the presence of oxygen on oxygen-precovered Cu<sub>2</sub>O(111) surface, compared with clean Cu<sub>2</sub>O(111) surface, obviously improve the catalytic activity of Cu<sub>2</sub>O for CH<sub>3</sub>OH decomposition, and reduce the activation barrier of O–H bond cleavage. Meanwhile, the O–H bond-breaking pathway of CH<sub>3</sub>OH on oxygen-precovered Cu<sub>2</sub>O(111) surface is the most favorable pathway for the formation of CH<sub>3</sub>O, which indicates that the O atom of CH<sub>3</sub>O is from O of CH<sub>3</sub>OH, not from the oxygen-precovered. That is to say, oxygen acts as a promoter for the formation of CH<sub>3</sub>O by CH<sub>3</sub>OH decomposition on oxygen-precovered Cu<sub>2</sub>O(111) surface.

### Acknowledgements

The authors thank the anonymous reviewers for their helpful suggestions on the quality improvement of our present paper. This work was supported by the National Basic Research Program of China (2005CB221204), and the National Natural Science Foundation of China (No. 20906066, 20976113 and 20976115).

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