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Insights into the reaction mechanisms of methanol decomposition, methanol oxidation and steam reforming of methanol on Cu(111): A density functional theory study

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ABSTRACT

Cu-based catalysts have been widely used for hydrogen production from methanol decomposition, methanol oxidation and steam reforming of methanol (MSR). In this study, we have systematically identified possible reaction paths for the thermodynamics and dynamics involved in the three reactions on a Cu(111) surface at the molecular level. We find that the reaction paths of the three reactions are the same at the beginning, where methanol scission is favourable involving O–H bond scission followed by sequential dehydrogenation to formaldehyde. Formaldehyde is an important intermediate in the three reactions, where direct dehydrogenation of formaldehyde to CO is favourable for methanol decomposition; for methanol oxidation, formaldehyde tends to react with oxygen to form dioxymethylene through C–H bond breaking and finally the end products are mainly CO₂ and hydrogen; for MSR, formaldehyde tends to react with hydroxyl to form hydroxymethoxy through formic acid and formate formation, followed by dissociation to CO₂. CH₂O formation from methoxy dehydrogenation is considered to be the rate-limiting step for the three reactions. In general, the thermodynamic and kinetic preference of the three reactions shows the order methanol oxidation > MSR > methanol decomposition. Methanol oxidation and MSR are faster than methanol decomposition by about 500 and 85 times at typical catalytic conditions (e.g., 523 K), respectively. The result may be useful for computational design and optimization of Cu-based catalysts.

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1. Introduction

Recently, alternative energy sources have received great attention due to the decline of fossil fuel resources and their

increasing cost [1]. Methanol is the smallest alcohol molecule, and is being studied as a viable alternative to commercial fossil fuel resources. To be used as a clean fuel, methanol is often first transferred into hydrogen [2]. There are three primary ways to realize such a transfer; methanol decomposition

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($\text{CH}_3\text{OH} = \text{CO} + 2\text{H}_2$) [3–5], methanol oxidation ($\text{CH}_3\text{OH} + 1/2\text{O}_2 = \text{CO}_2 + 2\text{H}_2$) [6–8] and methanol steam reforming (MSR, $\text{CH}_3\text{OH} + \text{H}_2\text{O} = \text{CO}_2 + 3\text{H}_2$) [9–12]. Due to the importance of hydrogen, much attention has been paid to methanol dissociation on transition metal surfaces, such as Pt [13–16], Pd [17–20], Cu [18,21–24], Ir [25,26] and various alloys [2,20,27,28].

There are three types of catalysts for methanol decomposition; Pt-, Pd- and Cu-based catalysts [4,5,7–12,27]. However, the application of Pt- and Pd-based catalysts is restricted because Pt and Pd are precious metals. Therefore, much interest and concern have been focused on the study of methanol scission on Cu-based catalysts [7–9,12]. Previous work involving methanol decomposition on the Cu(110) surface finds that a number of preadsorbed CH_3OH and small amounts of CH_2O desorb from the surface after heating, indicating that clean Cu(110) is not very active in methanol dissociation. However, when the surface is covered by O atoms, methanol dissociation is significantly facilitated, and various products have been observed, such as H_2O , H_2 and CH_2O [29–34]. The reaction mechanism of methanol dissociation is described as first involving O–H bond scission in methanol followed by sequential dehydrogenation to CH_2O , then to CO or CO_2 .

Previous theoretical calculations have been performed to investigate methanol decomposition on Cu(111), (110) and (100) surfaces. Greeley and Mavrikakis found that the most favourable route for methanol direct scission on a clean Cu(111) surface is described as follows: $\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} \rightarrow \text{CH}_2\text{O} \rightarrow \text{CHO} \rightarrow \text{CO}$, and methoxy dehydrogenation is the rate-limiting step [23]. Mei et al. also found the same reaction mechanism on a clean Cu(110) surface [21]. Sakong and Gross proposed that methanol oxidation may proceed through $\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} \rightarrow \text{CH}_2\text{O} \rightarrow \text{CH}_2\text{OO} \rightarrow \text{CHOO} \rightarrow \text{CO}_2$, in which CHOO dehydrogenation is the rate-limiting step [22,35]. For MSR, Bo et al. studied CH_2O dissociation on hydroxyl-covered and oxygen-covered Cu(100) surfaces, and found that formaldehyde reaction with surface O atoms is thermodynamically more favourable compared with the reaction path of formaldehyde with OH [36]. Gu and Li studied methanol dissociation on a hydroxyl-covered Cu(111) surface, and found that CH_2O tends to react with hydroxyl to form hydroxymethoxy followed by its dissociation to CO_2 [18]. However, they consider that preadsorbed OH only reacts with CH_2O , and do not study OH reaction with other intermediates. To the best of our knowledge, a detailed understanding of the mechanism of MSR is still lacking.

It has been generally agreed that the active component in Cu-based catalysts for various reactions, including methanol decomposition, methanol oxidation and MSR, is metallic copper [18,37]. Meanwhile, X-ray diffraction (XRD) characterization has proven that Cu(111) is the main component on the surface of copper [38,39], and has been widely used in previous theoretical investigations regarding molecule adsorptions on transition metal surfaces [20,21,24,40,41]. In the paper, we have systematically identified possible reaction paths for the thermodynamics and dynamics involved in the steam reforming of methanol on a Cu(111) surface at the molecular level. In order to better understand the differences of underlying mechanism for the three reactions and give a guide to the rational design of Cu-based catalysts, methanol

decomposition and methanol oxidation are also studied on Cu(111) surface using density functional theory (DFT).

2. Calculation models and methods

All calculations were performed using the Dmol³ package in Material Studio [42,43], which has already been extensively used to study CO_2 hydrogenation on Cu surfaces [44,45], H_2S desulfurization on ZnO surfaces [46,47], and water gas shift reaction on Au surfaces [48,49]. The all-electron relativistic DFT [42,43] was used for core electrons by employing the generalized gradient approximation and the Perdew and Wang function (PW91) [50]. The electronic structures were obtained by solving the Kohn–Sham [51,52] self-consistent equation under an unrestricted spin condition. Furthermore, the double-numerical atomic orbital basis set plus polarization function was used.

The transition states (TSs) were derived by using the complete linear synchronous transit (LST)/quadratic synchronous transit (QST) method [53]. The linear synchronous transit (LST) maximization was performed, followed by an energy minimization in the directions leading to the reaction pathway. The TS approximation obtained in that way is used to perform a QST maximization. From that point, another conjugate gradient minimization is performed. The cycle is repeated until a stationary point is located or the number of allowed QST steps is exhausted.

A Cu(111) surface is cleaved from the face-centred cubic (fcc) crystal structure after optimization, and the theoretical equilibrium lattice constant of Cu is $a_{\text{Cu}} = 3.685 \text{ \AA}$ compared with the experimental value of $a_{\text{Cu}} = 3.604 \text{ \AA}$ [54]. The surface is modelled using a four-layered $p(4 \times 4)$ super cell with sixteen atoms in each layer, and a 15 Å vacuum slab is employed to separate the periodically repeated slabs. In all calculations, the copper atoms on the top two layers with the adsorbates were allowed to relax, whereas the other layers were fixed, and volume was maintained constant. The molecules in the gas phase are calculated using a $10 \times 10 \times 10 \text{ \AA}^3$ cubic unit cell. As shown in Fig. 1, there are four different adsorption sites on the Cu(111) surface; top (T), bridge (B), fcc and hexagonal close-packed (hcp).

For methanol oxidation, the O_2 molecule will be dissociated into two O atoms, and then react with other adsorbate (adsorption methanol or possible intermediates); For steam reforming of methanol, the H_2O molecular will be dissociated into OH and H, or O and H and then O or OH will react with other adsorbate. Therefore, the adsorption of adsorbate, co-adsorption of O and adsorbate and OH and adsorbate are studied. The adsorption energies (E) are defined as follows:

For a single adsorbate adsorption,

$$E = E_{\text{Cu}(111)+\text{adsorbate}} - E_{\text{Cu}(111)} - E_{\text{adsorbate}}$$

For the co-adsorption of adsorbate and X (O or OH),

$$E = E_{\text{Cu}(111)/\text{X}+\text{adsorbate}} - E_{\text{Cu}(111)/\text{X}} - E_{\text{adsorbate}}$$

where $E_{\text{Cu}(110)}$ and $E_{\text{Cu}(111)/\text{X}}$ are the energies of a clean and preadsorbed O or OH Cu(111) surface, respectively; $E_{\text{Cu}(111)+\text{adsorbate}}$ and $E_{\text{Cu}(111)/\text{X}+\text{adsorbate}}$ are the total energies of

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