Partial oxidation of methanol on Cu(110): energetics and kinetics

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The reaction pathway of the partial oxidation of methanol to formaldehyde on clean and oxygen-precovered Cu(110) has been studied by density functional theory calculations within the generalized gradient approximation. Dosing the Cu surfaces with oxygen promotes the methanol oxidation by stabilizing the methoxy intermediate on Cu and inducing the removal of surface hydrogen via water desorption. Using the information from the total-energy calculations in kinetic Monte Carlo simulations, the temperature programmed desorption of methanol was addressed thus yielding information on the microscopic details of the oxidation kinetics and the accuracy of the calculated barriers.

I. INTRODUCTION

The interaction of methanol with low-index copper surfaces has been a model system for the study of alcohol adsorption on metal surfaces [1–13]. These studies were also motivated by the important role of copper in the synthesis and steam reforming of methanol. Industrially, methanol synthesis and decomposition are promoted by Al_2O_3-supported Cu/ZnO catalysts [14]. However, the precise state of the copper and the role of the ZnO in the Cu/ZnO-catalysts is still unclear. The active phase has been suggested to be either copper dissolved in the bulk [15] or metallic copper dispersed on the ZnO surface [16].

Our knowledge about the oxidation steps of methanol on Cu surfaces is mainly based on temperature programmed desorption (TPD) and scanning tunneling microscopy (STM) experiments. Clean copper surfaces are relatively inactive for methanol oxidation. At low surface temperatures of about 100 K only adsorbed methanol is present at Cu surfaces [1–3, 12]. Upon heating, first methoxy and then formaldehyde is formed [3, 12]. Further heating above 300 K leads to the desorption of formaldehyde and the associative desorption of hydrogen and methoxy as methanol.

It is well-known that the decomposition of methanol on copper is strongly promoted by the presence of oxygen [1, 3]. Methanol is converted to methoxy on copper predosed with oxygen via the formation of surface hydroxyl [13] at 130 K. High-resolution X-ray photoelectron spectra (HRXPS) recorded at 220 K [12] indicate that the adsorbed hydroxyl species then interacts with further methanol resulting in additional methoxy and water which then desorbs. If the oxygen coverage is kept low, the methoxy adsorbates are decomposed to form formaldehyde and atomic hydrogen at 330-400 K [1, 8]. For higher oxygen coverages, also the formation of formate is observed [6, 7, 17] which is followed by CO_2 production and desorption.

Electronic structure calculations so far focused on the methanol dehydrogenation on clean Cu(111) with the Cu substrate modeled by a finite cluster [18–20] of by a periodic slab [21], but also the clean Cu(100) substrate has been addressed by cluster calculations [22]. These calculations confirmed that the rate-limiting step in the methanol oxidation on clean copper is the methoxy decomposition which is hindered by a large barrier.

We have recently studied the partial oxidation of methanol on clean and oxygen-covered Cu(100) and Cu(110) in detail using periodic density functional theory (DFT) calculations [23]. We have shown that the promotion of the methanol oxidation on oxygen-covered copper surfaces is not caused by any significant reduction of the methoxy decomposition barrier; oxygen rather enhances the formaldehyde formation by stabilizing the methoxy intermediate and removing the hydrogen via water desorption.

Since recently it was suggested that the activity of methanol synthesis can be directly correlated with the microstrain of the copper metal particles [24, 25], we also studied strain effects in the adsorption on copper surfaces [23, 26]. For methanol on copper, we found that tensile strain leads to enhanced binding energies of the reaction intermediates, as also found in other systems [27–33]. However, there is no clear trend for a particular reaction barrier or energy difference as a function of the lattice strain [23].

In this contribution we focus on the methanol decomposition to formaldehyde on Cu(110). We will identify the reaction path and discuss the stability of the reaction intermediates. From the calculated reaction barriers, the rates for each reaction step have been estimated using transition state theory [34]. These rates have then entered a kinetic Monte Carlo (kMC) simulation of the temperature programmed desorption (TPD) of methanol from oxygen-covered Cu(110) which allows to follow the microscopic details of the reaction kinetics and to make a thorough comparison between theory and experiment.

II. THEORETICAL METHODS

The energetics of the methanol oxidation have been determined by periodic DFT calculations in the supercell approach using the Vienna *ab initio* simulation package (VASP) [35] and the Perdew-Wang (PW91) functional [36] to treat the exchange-correlation effects within the generalized gradient approximation (GGA).

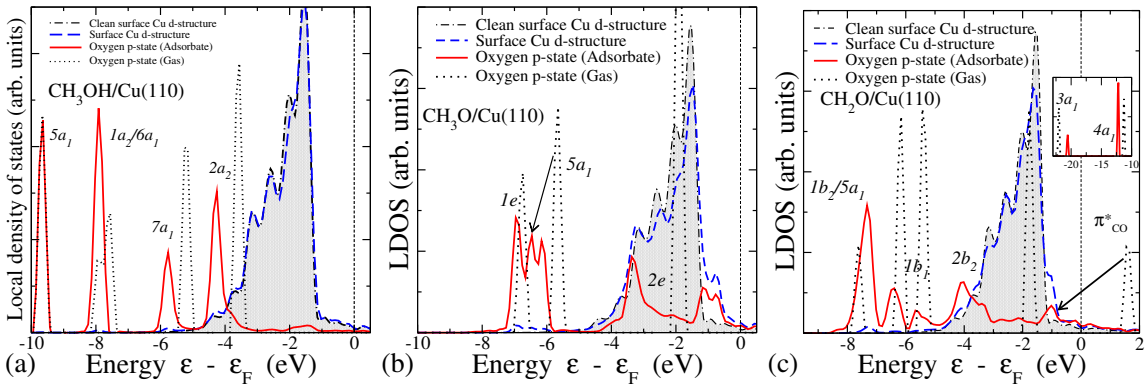

FIG. 1: Projected local density of states (LDOS) of the oxygen atom of (a) methanol, (b) methoxy and (c) formaldehyde on Cu(110). While the methanol orbitals are just slightly shifted downwards, the methoxy and formaldehyde orbitals are strongly perturbed due to the interaction with the Cu substrate.

The ionic cores are representated by ultrasoft pseudopotentials [37, 38], and the plane wave basis has been expanded up to an cutoff energy of 350 eV which causes an error of less than 10 meV in the calculated binding energies. The Cu substrate was modeled by a periodic array of 5-layer slabs separated by 12 Å vacuum with the two uppermost Cu layers fully relaxed. The total energies have been evaluated by summing up over a Monkhorst-Pack **k**-point mesh of 16×16×1 for the 2×2 surface unit cells mainly employed in this study. The orbital projected local density of states (LDOS) has been analysed in order to determine the nature of the chemical bonding between the reaction intermediates and the substrate. In the assignment of the molecular orbitals we have followed the general quantum chemistry naming rules.

The minimum energy paths are determined by using the climbing image nudged elastic band (NEB) method [39] and also the dimer method [40] in order to determine the geometries of the transition states. The rates for the reaction steps have been derived from the calculated barrier heights by using transition state theory [34] and assuming a generic prefactor of $\nu_0 = 10^{12} s^{-1}$. The kinetic Monte Carlo simulations have been performed as for example described in Ref. [41]. A grid of 60×60 sites with periodic boundary conditions has been used to model the substrate. The details of the kinetic Monte Carlo simulations will be discussed in a forthcoming publication [42].

III. RESULTS

A. Energetics

As a first step, we determined the energetically most favorable adsorption sites of the reaction intermediates methanol, methoxy and formaldehyde in the partial oxidation of methanol on Cu(110). Their adsorption energies are listed in Table I where also their adsorption geometries are characterized by the position of the oxygen, hydroxyl hydrogen and carbon atom of the respective molecule within the surface unit cell. Furthermore, the projected local density of states (LDOS) of the molecular orbitals and the Cu *d*-bands are plotted in Fig. 1 in order to analyse the bonding between the molecules and the substrate.

Methanol is relatively weakly bound to Cu(110) at a distance more than 2 Å away from the uppermost Cu plane. The hydroxyl bond (O-H) of methanol is oriented parallel to the surface and the C-O bond is almost upright. The weak interaction is confirmed by the analysis of the electronic structure in Fig. 1a. The molecular orbitals of methanol are just slightly shifted down and the Cu *d*-band is hardly perturbed by the presence of methanol so that methanol can be regarded as being physisorbed on Cu(110).

In the case of the adsorption of the open-shell methoxy radical (CH_3O), the situation is entirely different. The non-bonding $2e$ orbital that is only partially filled in the gas-phase [43] becomes significantly broadened upon adsorption. Furthermore, the p_z ($5a_1$) orbital is shifted down considerably to a position between the p_x and p_y ($1e$) peaks. These are no longer degenerate due to the low-symmetry situation of the methoxy adsorption position at the short bridge site. The CO bond is tilted by 33° along [001] from the (110) surface normal which

Adsorbate	Site	$E_{\rm ads}$(eV)	$h_{\rm Cu-O}$(Å))
CH_3OH	O_t-H_{lb}	−0.41	2.02
CH_3O	O_{sb}	−2.98	1.44
CH_2O	C_b-O_b	−0.70	1.42

TABLE I: Molecular adsorption energies $E_{\rm ads}$ and adsorption height of the oxygen atom $h_{\rm Cu-O}$ with respect to the uppermost Cu plane for methanol, methoxy and formaldehyde at the most favorable adsorption position on Cu(110) in a $p(2\times2)$ geometry. The adsorption sites are characterized with respect to the oxygen, hydroxyl hydrogen and carbon position within the surface unit cell. *t*, *b* and *sb* denote the top, bridge and the short-bridge sites of the (110) surface, respectively.

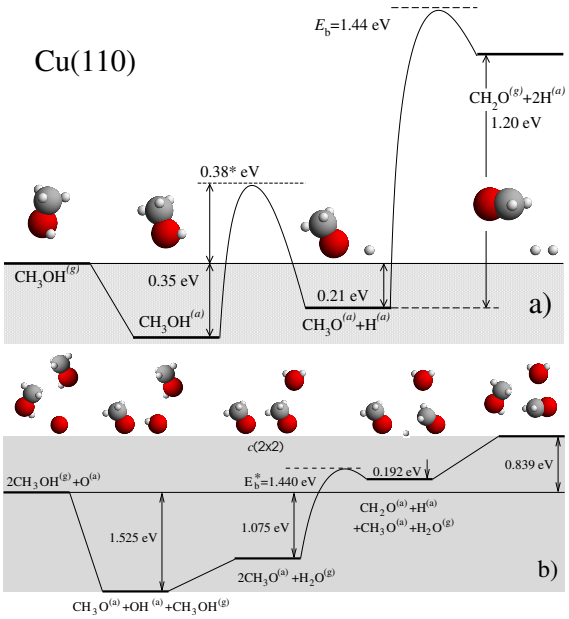

FIG. 2: Reaction pathways of the methanol decomposition on clean (a) and oxygen-covered (b) Cu(110). See the text for a description of the configurations of the reaction intermediates.

can be described as a pseudo (111) surface edge position. This strong interaction leads to a large adsorption energy of −2.98 eV.

The closed-shell species formaldehyde is again relatively weakly bound on Cu(110). However, the local density of states (Fig. 1c) is also strongly modified upon the interaction with the Cu substrate. The resulting molecular electronic structure resembles the one of adsorbed methoxy. Furthermore, the σ_{C-O} ($3a_1$) and σ_{CH_2} ($4a_1$) orbitals (see the inset of Fig. 1c) are shifted to positions adequate for methoxy. And indeed, the adsorption configuration of the this η^2-formaldehyde can be interpreted as a formaldehyde molecule within the geometry of a free methoxy radical except for the missing methyl hydrogen atom. The CO bond is oriented parallel to the surface and elongated from 1.22 Å in the gas phase to 1.41 Å close to the corresponding value of methoxy. This elongation of the π_{C-O} bond is reflected by the strong decrease in the intensity of the corresponding $1b_1$ peak. In addition, the $1b_2$ orbital is strongly hybridized with the Cu *d*-band reflecting the strong interaction between the formaldehyde and the substrate.

Still the adsorption energy of this formaldehyde species is modest in spite of the strong interaction. This is caused by the significant deformation of the adsorbed formaldehyde which requires 1.65 eV in the gas-phase. This energetic cost counteracts the energy gain upon adsorption.

The reaction pathways in the partial oxidation of methanol on clean and oxygen-covered Cu(110) are illustrated in Fig. 2. Within a (2×2) unit cell, there is still a repulsive interaction between the reaction products, namely the hydrogen atoms and adsorbed methoxy and formaldehyde, respectively. For the energies of the intermediate states shown in Fig. 2, we have assumed that the coadsorbates are in fact separated infinitely from each other so that there is no interaction.

On clean Cu(110), the first oxidation step, the O-H bond scission for methanol located above the short-bridge position is hindered by a barrier of about 0.7 eV. However, the rate-limiting step in the oxidation of methanol is the C-H bond scission which requires an activation energy of 1.44 eV according to the DFT-GGA calculations. At the barrier position, the CO bond length is already strongly reduced to the value for adsorbed formaldehyde. Furthermore, the C-H bond is elongated to 2.28 Å, i.e. the barrier is at a so-called late position [44].

With respect to the high barrier for the C-H bond scission it is surprising that still formaldehyde is formed from methoxy on clean Cu surfaces [1, 12]. However, one has to take into account that the desorption of methoxy requires the presence of hydrogen. Since there is a repulsive interaction between the adsorbed hydrogen atoms and methoxy and due to the fact that the associative desorption of H_2 has a comparable but lower desorption barrier on Cu [26, 45, 46], hydrogen rather desorbs than reacts with methoxy, as confirmed by our kinetic simulations. Thus the associative desorption channel becomes unavailable for adsorbed methoxy. Only if there is a high concentration of hydrogen present at the surface, methoxy desorbs associatively as methanol [1].

As for oxygen-covered Cu(110), it is experimentally well-established that this surface exhibits a (2×1) "added row" reconstruction consisting of Cu-O-Cu chains [47, 48]. Still we first considered "isolated" oxygen adatoms in a $p(2\times2)$ structure on Cu(110) surface so that first the results might also be relevant for more open structures as in real catalysts [25], and second, because it is known that the methanol oxidation is active on the edges of oxygen (2×1) islands [10, 11]. The initial steps of the methanol oxidation on $p(2\times2)$O/Cu(110) are illustrated in Fig. 2b. On such a surface, methanol spontaneously dissociates into adsorbed methoxy and hydrogen that forms a surface hydroxyl with the adsorbed oxygen atom. This process leads to a large energy gain of 1.53 eV. An amount of 0.31 eV of this energy is due to the attractive interaction between methoxy and OH within the $p(2 \times 2)$ unit cell compared to the isolated adsorbates.

The second oxidation step, the C-H bond scission, is hardly affected by the presence of oxygen. On the (2×1) oxygen-covered Cu(110) surface this barrier is reduced from 1.44 eV to 1.30 eV. However, the stabilisation of the methoxy intermediate already promotes the further methanol oxidation since adsorbed methoxy rather decomposes than desorbs because of the large desorption barrier. However, STM experiments have revealed that Cu(110) exposed to mixtures of oxygen and methanol forms separated oxygen-covered and methoxy-covered areas. The methoxy-covered regions consists of zigzag chains and $c(2 \times 2)$ structures [4, 10, 11]. Our calculations confirm that the methoxy $c(2 \times 2)$ structure is

stabilized by 0.1 eV per molecule with respect to the $p(2 \times 2)$ structure.

Therefore we have considered the additional dissociative adsorption of methanol in the (2×2) unit cell forming a $c(2 \times 2)$ methoxy structure plus one adsorbed water molecule. This process requires an energy cost of 0.41 eV. However, there is basically no barrier for the water desorption from this structure so that the overall reaction

$$2CH_3OH^{(g)} + O^{(a)} \longrightarrow 2CH_3O^{c(2\times2)} + H_2O^{(g)}. \quad (1)$$

is exothermic by 1.08 eV. As for the further oxidation steps, the TPD experiments [1] showed that both methanol and formaldehyde are produced simultaneously at temperatures between 350 K and 375 K according to the reaction scheme

$$2CH_3O^{c(2\times2)} \longrightarrow CH_3OH^{(g)} + CH_2O^{(g)} . \quad (2)$$

Our DFT calculations yield that this process requires an energy of 1.9 eV (see the last two reaction steps in Fig. 2b).

B. Kinetics

As discussed in the previous section, the reaction pathways determined by the DFT calculations are qualitatively in agreement with the experimental findings. However, the static information obtained from the energetics along the reaction path is not sufficient for a quantitative comparison with experiments. Only a realistic simulation of the experimental situation allows such a comparison. Therefore, we have performed kinetic Monte Carlo simulations of the temperature programmed desorption of methanol from oxygen-covered Cu(110). Thus we also obtain a detailed microscopic insight in the reaction kinetics of the methanol oxidation on Cu(110).

The kMC simulations were performed on a rectangular grid of 60 × 60 sites with periodic boundary conditions. The surface was precovered with 0.25 ML oxygen, and then a methanol flux of 0.1 ML/s was applied for 100 s at a temperature of 100 K. After this exposure, the surface was covered with CH_3OH, CH_3O and OH, the latter products coming from the spontaneous dissociative adsorption of methanol on $p(2 \times 2)$O/Cu(110). The concentration of methanol and methoxy was 55 % and 20 %, respectively. Subsequently, the temperature programmed desorption was modeled with a heating rage of 5 K/s.

Using the original DFT energy barriers, methanol starts to desorb at 145 K whereas formaldehyde is formed for temperatures higher than 500 K and desorbs. As soon as the methoxy reacts to formaldehyde at 500 K, hydrogen atoms are created on the surface. These atoms can react with the adsorbed methoxy to methanol or, if two hydrogen atoms are next neighbours, they can associatively desorb. Thus methanol, formaldehyde and hydrogen all desorb in the same temperature range, as was also found in TPD experiments [1].

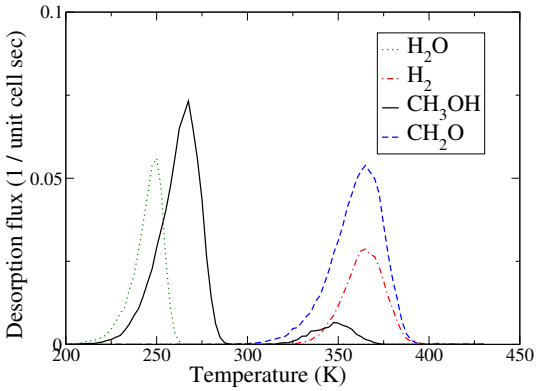

FIG. 3: Kinetic Monte Carlo simulation of the temperature-programmed desorption spectrum of methanol adsorbed on oxygen-covered Cu(110) based on DFT results. The methanol adsorption energy and the C-H bond scission barrier have been adjusted in order to reproduce the experimental spectrum.

However, there are quantitative differences between simulation and experiment. Experimentally, the initial methanol desorption only starts at 190 K whereas formaldehyde formation already occurs at 350 K. This means that the calculated adsorption energy of methanol is too low while the calculated barrier for the C-H bond scission is too high. The overestimation of C-H bond scission barriers by GGA-DFT calculations is already well-known for other systems [49, 50].

In order to get a better agreement of the simulated TPD spectra with the experiment, we increased the methanol binding energy on Cu(110) to 0.65 eV while the barrier for the methoxy decomposition was reduced to 0.90 eV. Using these modified barriers, we obtained the TPD spectrum shown in Fig. 3. In fact, the adjusted methanol binding energy and the C-H bond scission barrier agree also very well with the corresponding experimentally derived values of 0.70 eV [1] and 0.92 eV [5], respectively. Now the experimental ordering of the peaks and the peak temperatures are well-reproduced. The water which starts to desorb at about 210 K is formed in the reaction (1). At slightly higher temperatures methanol desorbs until only methoxy is present at the surface which starts to be dehydrogenated at about 310 K.

The magnitude of the different desorption peaks after the methoxy decomposition is also in satisfactory agreement with the experiment. In order to obtain a significant H_2 desorption flux it is essential to include the calculated repulsive interaction of methoxy and hydrogen of about 0.3 eV, as mentioned in the last section. Otherwise, hydrogen would predominantly desorb associatively with methoxy whose surface concentration is much higher than the one of hydrogen.

There are still remaining discrepancies between the calculated and measured TPD spectra. In particular, the width of the calculated peaks is much smaller compared to the experimental peaks. This is caused by the fact that

we neglected most of the lateral interactions between the adsorbates in our simulations [41]. To compute these interactions would require a high computational effort. We neglected these interactions because we were mainly interested in the temperatures of the desorption maxima which are hardly modified by the inclusion of this interaction.

IV. CONCLUSIONS

The partial oxidation of methanol on clean and oxygen-covered Cu(110) has been addressed by density functional theory calculations and kinetic Monte Carlo simulations. The rate-limiting step in the partial oxidation of methanol is the decomposition of methoxy into formaldehyde and hydrogen. This barrier is not reduced by the presence of oxygen on the surface, but oxygen still enhances the formaldehyde formation by stabilizing the methoxy intermediate and removing the hydrogen via water desorption. The simulated temperature programmed desorption spectra are in good agreement with the experiment once the calculated DFT methanol adsorption energy is increased and the methoxy dehydrogenation barrier is reduced.

Acknowledgments

This work has been supported by the German Academic Exchange Service (DAAD) and the German Science Foundation (DFG, GR1503/12-1).

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