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Reaction intermediates of methanol synthesis and the water–gas-shift reaction on the ZnO(0001) surface

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ABSTRACT

The polar Zn-ZnO(0001) surface is involved in the catalysis of methanol synthesis and the water–gas-shift reaction. We use density functional theory calculations to explore the favorable binding geometries and energies of adsorption of several molecular species relevant to these reactions, namely carbon monoxide (CO), carbon dioxide (CO_2), water (H_2O) and methanol (CH_3OH). We also consider several proposed reaction intermediates, including hydroxymethyl (CH_2OH), methoxyl (CH_3), formaldehyde (CH_2O), methyl (CH_3), methylene (CH_2), formic acid (HCOOH), formate (HCOO), formyl (HCO), hydroxyl (OH), oxygen (O) and hydrogen (H). For each, we identify the preferred binding geometry at a coverage of 1/4 monolayers (ML), and report calculated vibrational frequencies that could aid in the identification of these species in experiment. We further explore the effects on the binding energy when the adsorbate coverage is lowered to 1/9 and 1/16 ML.

1. Introduction

Methanol (CH_3OH) is industrially important in the synthesis of various chemicals and is also predicted to play a key role in the next generation of renewable energy sources for use in fuel cells [1,2], or potentially as a medium for hydrogen storage and transportation. Industrially, methanol is mass produced using alumina-supported ZnO catalysts [3,4]. In addition, ZnO also catalyses the forward and reverse water–gas-shift reaction [5]. As a consequence, there is much interest in studying the detailed chemical mechanisms of methanol synthesis and the water–gas-shift reaction on ZnO surfaces.

In an early study, Ueno et al. [6] used infrared spectroscopy to study the reaction intermediates of the water–gas-shift reaction on ZnO. They suggested that when a mixture of carbon dioxide and hydrogen is introduced over ZnO, the formate ion (HCOO) is formed. These reaction formates later decomposed to CO (dehydration) and CO_2 (dehydrogenation). Ueno et al. [7] also studied the reaction of methanol decomposition on ZnO using infrared spectroscopy. By introducing methanol over ZnO, the methoxyl ion (CH_3O) and the formate ion (HCOO) are observed, while H_2, CO_2 and CO are evolved into the gas phase. They suggest that CO is produced mainly by formate decomposition while H_2 and CO_2 are from the reaction between methanol and formate. Bowker et al. [8] used temperature programmed desorption (TPD) and temperature programmed reaction spectroscopy (TPRS) to study the adsorption and interaction of intermediate species such as H_2, H_2O, CO, CO_2, formaldehyde (CH_2O) and methanol (CH_3OH) over ZnO. They propose that the formate ion (HCOO) is the pivotal intermediate of ZnO catalysing methanol synthesis and can decompose to CO and H_2. Chadwick and Zheng [9] use TPD to study the decomposition of methanol on ZnO. They suggest that the decomposition products are mainly CO and H_2 with a small amount of CO_2. In addition, the influence of the H_2O molecule on methanol decomposition is investigated. Their results suggest that methanol, together with coadsorbed water molecules, enhances the formation of CO_2 and H_2. Bowker et al. [10] perform investigations into the crystal plane dependence of adsorption and reaction of CO, CO_2, H_2 and CO_2/H_2 co-adsorption on ZnO. They suggest that these processes are confined to the polar surfaces of ZnO. Vohs and Barteau [11] also confirm that the Zn-terminated ZnO(0001) surface is active for the decomposition reactions of methanol, formaldehyde, and formic acid.

In a more recent study, the mechanisms of methanol synthesis and the water–gas-shift reaction on ZnO were investigated by Tabatabaei et al. [5]. Infrared spectroscopy and TPD resolve two types of formate species during the coadsorption of CO_2 and H_2 on ZnO. For temperatures below 500 K, they suggest that a bidentate formate is formed which decomposes to CO_2 and H_2. For temperatures above 500 K, a monodentate formate is present which decomposes into CO and H_2. After the forward water–gas-shift reaction, only bidentate formate is identified from the TPD analysis. Their further TPD analysis shows that both the reverse water–gas-shift reaction and methanol synthesis occur concurrently, with the existence of both types of formates. Therefore, they suggest that the monodentate formate is the principal intermediate

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for methanol synthesis while the bidentate formate is the intermediate responsible for the forward and reverse water–gas-shift reactions.

The above-mentioned studies of methanol decomposition on ZnO suggest that the main catalytic intermediates are the methoxyl and formate, whereas in the water–gas-shift reaction, only formate appears to be a critical intermediate. The main catalyst for the water–gas-shift reaction and methanol synthesis is Cu/ZnO, i.e. the addition of Cu to zinc-oxide [12–14]. At present, however, the role of the oxide, as well as the actual mechanism by which the copper metal activates the reactions, is still unclear. For example, oxygen vacancies on ZnO(000 1) have recently been proposed to be the catalytically active sites for methanol synthesis on pure ZnO, where the charge state of the vacancy is also understood to affect the chemical activity [15]. With regard to the (0001) Zn-terminated surface studied in the present work, before the effect of copper, and other defects, on catalyst activity can be examined, the behaviour of the adsorption of intermediates on the clean zinc-oxide surface must be established as a reference.

In the present paper, we provide insights into the preferred binding geometries, adsorption energies, and associated vibrational frequencies for various possible molecular and atomic intermediates on the ZnO (0001) surface that may be of relevance for, and help in the understanding of, various heterogeneous catalytic reactions such as methanol synthesis and the water–gas-shift reaction. The gross-mechanisms involved, e.g. in methanol formation from syngas are $CO+2H_2 \leftrightarrow CH_3OH$, $CO_2+3H_2 \leftrightarrow CH_3OH+H_2O$, and $CO+H_2O \leftrightarrow CO_2+H_2$, the latter being the water–gas-shift reaction. The polarity of the oxide is expected to play an important role in catalysis. For understanding the behaviour and function of a catalyst, it is necessary to consider all the main low energy surfaces. We choose to begin with the Zn-terminated ZnO(0001) orientation because there is recent detailed quantitative information regarding the atomic structure for the clean surface [16] which is very helpful, if not mandatory, for investigation of the properties of adsorption structures on a surface. There are also experimental measurements (scanning tunneling microscopy, low energy electron diffraction, ultraviolet photoelectron spectroscopy and low energy ion scattering) for the Cu/ZnO(0001) surface [17] which we are presently investigating theoretically.

Our results will complement and expand on earlier studies on the (0001) [18–20] and the (10$\bar{1}$0) surfaces [19]. Although some of the intermediate species considered here, such as hydroxymethyl (CH_2OH), methylene (CH_2) and the formyl (HCO), have not been directly detected in experiment, they may still occur as transient species in the catalytic process. The binding energies and atomic geometries of these transients represent important information, allowing one to assess their possible role in surface-facilitated chemical transformations.

2. Computational methodology

Self-consistent total-energy calculations are performed in the framework of all-electron density functional theory (DFT) as implemented in the DMol^3 code [21]. The Kohn–Sham eigenfunctions are expanded in terms of a numerical atom-centered basis set of double numerical plus polarization (DNP) quality with a radial cutoff of 9 bohr. Exchange and correlation are treated in the generalized gradient approximation (GGA) in the form of the Perdew, Burke, and Ernzerhof (PBE) functional [22]. Scalar-relativistic corrections are explicitly included in our treatment.

For bulk wurtzite ZnO we use a $10\times10\times10$ k-point grid and obtain the following lattice parameters: $a=3.302$ Å, $c=5.317$ Å, $c/a=1.610$, and $u=0.362$. The bulk modulus is calculated to be 117 GPa. These values agree very well with the results of other *ab initio* calculations by Meyer and Marx [23] also using the GGA-PBE functional; they obtain $a=3.282$ Å, $c=5.291$ Å, $c/a=1.6120$, and $u=0.3792$, and a bulk modulus of 128 GPa. The theoretical values agree well with experimental values [24–26]: $a=3.250$ Å, $c=5.207$ Å, $c/a=1.602$, and $u=0.3825$, and bulk modulus, 143 GPa.

The ZnO(0001) surface is represented using a three-dimensionally periodic slab model. The supercell contains four double layers of Zn–O and the adsorbed molecule, and is separated from its periodic image by 25 Å of vacuum. The surface of interest in this work is the Zn-terminated (0001) surface which is presented on one side of the slab only. The other slab surface, the O-terminated (000 1) surface, is electronically saturated using fictitious quasi-atoms with a nuclear charge of $e/2$. As discussed by Meyer and Marx [23], this quenches the residual internal electric fields in the slab. We restricted our slab to four (double) layers due to the need to balance accuracy with the ability to survey large number of configurations. Test showed that increasing the slab to size double layers results in an increase of the surface energy by only 0.034 eV per (1×1) cell. Integration over the Brillouin zone is performed using a 16×16 k-point mesh [27] for a (1×1) surface unit cell. Correspondingly smaller grids are used for larger surface unit cells. In our slab geometry optimisations, the unit cell dimensions as well as the positions of the Zn–O double layer furthest from the (0001) surface are held fixed at bulk values.

We investigate the adsorption on ZnO(0001) for a number of atoms and molecules relevant to the water–gas-shift reaction and methanol synthesis. These include CH_3OH, CH_2OH, CH_3, CH_3, CH_2, HCOOH, HCOO, HCO, H_2O, CO_2, CO, OH, O, and H. The adsorption energies are calculated using the following expression,

$$E_{\text{ads}} = -(E_{\text{surf}+\text{mol}} - E_{\text{surf}} - E_{\text{mol}}), \tag{1}$$

where $E_{\text{surf}+\text{mol}}$ is the total energy of the adsorbate/substrate system, E_{surf} is the total energy of the clean surface and E_{mol} is the total energy of the isolated (i.e. gas phase) molecule. As defined here, a more positive value of E_{ads} corresponds to a more stable configuration.

In order to ascertain that the most stable binding geometry is found for each molecule, we conduct an extensive survey over numerous conceivable configurations. This structure survey is carried out using a (2×2) surface unit cell (i.e. a coverage of 1/4 ML). For the case of the methanol molecule, for example, 16 configurations were tested. These are derived by placing the molecule in four orientations over the four high-symmetry binding sites on the surface, namely, the on-top site, the face-centered cubic (fcc) site, the hexagonal close-packed (hcp) site, and the bridge site, as illustrated in Fig. 1. While not all trial structures lead to unique or stable configurations after optimisation, this approach provides a reasonable degree of certainty that the most stable binding geometry for the molecule is found. In setting up trial structures, we also take care not to place adsorbates on exact symmetry positions so as to allow them to relax into other geometries if these are preferred. For the preferred configuration at 1/4 ML, binding energies are also calculated at the lower coverages of 1/9 ML and 1/16 ML, using (3×3) and (4×4) surface unit cells.

For the most stable adsorbate configuration at 1/4 ML coverage, we also calculate the vibrational modes. Vibrational frequencies are calculated by diagonalizing the mass-weighted Hessian matrix, which is computed for the adsorbate molecule and the two top-most surface atomic layers. The matrix elements are calculated by a three-point numerical differentiation of the forces using finite atomic displacements of 0.01 bohr.

3. Results

3.1. The clean ZnO(0001) surface

The ZnO(0001) surface is well studied regarding its surface structure [16,28]. The surface has been shown to exhibit triangular pit reconstructions with the ZnO(0001) surface inside the pit. As a first step in our investigations we consider adsorption on the ideal