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Methanol adsorption and decomposition on ZnO$(10\bar{1}0)$ surface: A density functional theory study[☆]

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ABSTRACT

The adsorption and subsequent dissociative reaction of methanol (CH_3OH) on clean ZnO$(10\bar{1}0)$ surface were investigated using the density functional theory methods and the periodic slab models. There are three adsorption modes of methanol were investigated. Among the two initially-stable adsorbed CH_3OH structures, the pathways of methanol dissociation via bond scission of the O—H, C—H and C—O bonds to form methoxide, hydroxymethyl and methyl radicals, respectively, were examined. Several possible pathways for CH_3OH decomposition on the ZnO$(10\bar{1}0)$ surface were proposed. Our calculated results pointed out that the most favorable reaction pathway is $CH_3OH_{(a)} \rightarrow CH_3O_{(a)} + H_{(a)} \rightarrow CH_2O_{(a)} + 2H_{(a)} \rightarrow CH_2O_{(g)} + 2H_{(a)}$. In addition, the nature of the surface–methanol bonding was investigated through scrutiny of electron density difference (EDD) contour plot.

1. Introduction

Increasing regulations on the emission of air pollutants as well as the heavy dependence on fossil fuels have stimulated interest in alternative renewable green fuels. Methanol has been emerging as a clean energy resource which can be added in the conventional fossil fuels or used directly for transportation as a source of hydrogen [1,2]. Due to its intrinsic advantages such as a high H/C ratio, low sulfur content, and storage/dispense requirements comparable to those for existing liquid fuels, methanol is an effective carrier for hydrogen which is primarily used in the fuel cell systems [3–5]. In addition, compared to natural gas, methanol is much easier to transport to points where it can be utilized. Therefore, great efforts have been made to achieve an efficient in situ conversion of methanol (CH_3OH) to hydrogen, e.g., in direct CH_3OH fuel cells (DMFC) [6,7].

Over the past two decades, there have been number of studies performed on the adsorption and decomposition mechanism of CH_3OH over the solid surfaces Cu [8], Pt [9], Mo [10], Ru [11], Au [12], Ni [13], TiO_2 [14], Fe_xO_y [15], and other metal compounds [16,17]. Because of the mixed covalent/ionic aspects in the chemical bonding [18–21], ZnO has been known as a very active catalyst for many reactions including those involves CH_3OH. Moreover, among the oxide catalysts, ZnO exhibits the best performance for the steam reforming of ethanol, i.e., it can produce 97.7% H_2 and CO_2 from ethanol, which shows that the ZnO catalyst is extremely selective to the overall steam reforming reaction of ethanol [22]. According to this, we predict that the ZnO will be a good selection for methanol decomposition. Therefore, it is essential to investigate the adsorption and conversion of CH_3OH over the ZnO surface. To the best of our knowledge, there is no such study that have been performed theoretically in order to understand the reaction of CH_3OH on ZnO surface.

It is well-known that wurtzite ZnO crystal has polar ((0001) and $(000\bar{1})$) and non-polar ($(10\bar{1}0)$ and $(11\bar{2}0)$) surfaces [23–26]. In non-polar surface, the $(10\bar{1}0)$ surface is containing pairs of coordinatively unsaturated Zn(II) and oxide sites, and this has been the focus of many experiments, such as the copper deposition or substitution. Previously, it has been suggested that, the non-polar surface $(10\bar{1}0)$ takes up to almost 80% of the total surface area. Therefore, in the present study we considered this non polar surface $(10\bar{1}0)$ of ZnO for the reaction of CH_3OH.

It has been proved that theoretical techniques can serve as powerful tools to understand the elementary reactions [16,27,28]. As a result, here we used the first-principles density functional theory (DFT) and self-consistent periodic calculations to investigate the methanol adsorption on the ZnO$(10\bar{1}0)$ surface. We determined the most stable geometry of CH_3OH adsorbed on this ZnO$(10\bar{1}0)$

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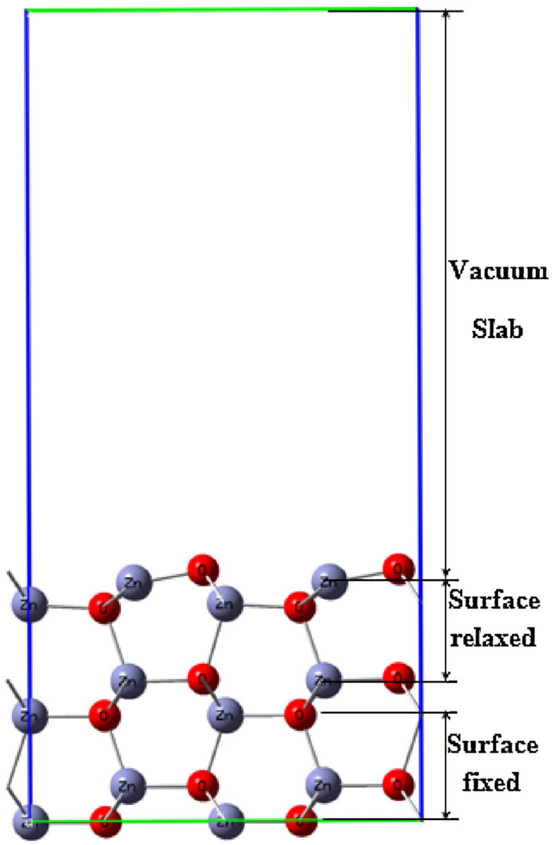

Fig. 1. The ZnO($10\bar{1}0$) surface model: two-dimensional view with 15 Å vacuum slab and six layers representation where the first two upper and the four bottom layers in the ($10\bar{1}0$) direction. The blue and red balls are Zn and O atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

surface and proposed herein the kinetically and thermodynamically favored channels leading to the final products. We also characterized the details of the interactions between CH_3OH and the surface by carrying out the analysis of the electron density difference (EDD).

2. Computational details

All DFT calculations were performed with the Vienna ab initio Simulation Package (VASP) [29–31]. The generalized gradient approximation was used with the functional described by Perdew and Wang (GGA-PW91) [32,33]. Electron–ion interactions were investigated with the use of the projector augmented wave method [34], and we performed non spin-polarized calculations for all of the structural optimizations. Normal-mode analysis was performed to verify the nature of each of these stationary points.

The ZnO($10\bar{1}0$) surface was modeled as a two-dimensional slab in a three-dimensional periodic cell. A (2 × 2) surface slab has thickness of six layers in which the top three layers were relaxed and the bottom three layers were fixed during the calculations (as shown in Fig. 1). In order to curtail the interaction between the slabs, we introduced a 15 Å of vacuum space in the *z* direction. The calculations were carried out using the Brillouim zone sampled with (4 × 4 × 4) and (4 × 2 × 1) Monkhorst–Pack [35] mesh *k*-points grid for ZnO bulk and all of ZnO($10\bar{1}0$) surface calculations, respectively.

The adsorption energy, E_{ads}, was calculated as follows

$$E_{ads} = E_{adsorbate/ZnO} - E_{adsorbate} - E_{ZnO} \qquad (1)$$

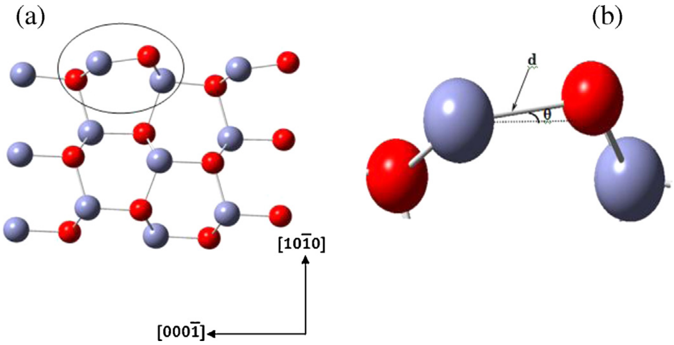

Fig. 2. A side view of relaxation and reconstruction on ZnO($10\bar{1}0$) surface, in which Fig. 2(a) shows six layer structure; 2(b) is an extraction (bordering by the dashed circle) from 2(a) to describe the relaxed surface. Compared to its bulk structure, the surface Zn—O bond tilts, marked with parameter *θ* and the bond linked between the surface zinc and oxygen contracts shown by *d*.

where, E_{ads} is the adsorption energy of the adsorbate, CH_3OH, on ($10\bar{1}0$)ZnO surface; $E_{adsorbate/ZnO}$ is the total energy of the optimized adsorbate on ZnO, $E_{adsorbate}$ is the total energy of the adsorbate, and E_{ZnO} is the total energy of the clean ZnO($10\bar{1}0$) slab. The nudged elastic band (NEB) method [36–38] was applied to locate the each transition state (TS), and all the TSs had been characterized as real first-order saddle points.

3. Results and discussion

3.1. Surface model

In order to validate our present model, we optimize the wurtzite ZnO bulk using the *k*-point mesh of 4 × 4 × 4 and cut off energy of 380 eV, and the calculated lattice constants *a* and *c* are 3.24 Å and 5.19 Å, respectively, which are in good agreement with previous values reported by Meyer and Marx [19] (3.25 and 5.20 Å, respectively). For the periodic system, slab calculation was implemented for non-polar surfaces with 15 Å vacuum regions to avoid interactions among periodic images. The geometric optimization of the surface dimer is described using the parameters as shown in Fig. 2 and Table 1.

The stoichiometric ZnO($10\bar{1}0$) surface is auto-compensated since it contains an equal number of zinc and oxygen atoms per unit area, and only one bond per atom is broken when the surface is created. The step-edge Zn and O atoms have one dangling bond per atom. Zn and O atoms of the surface form dimer rows running along the ($000\bar{1}$) direction [19,23]. Well-defined rectangular terraces are formed on the surface whose model is shown in Fig. 2(a). Steps formed by polar and non-polar faces run along the ($10\bar{1}0$) and ($000\bar{1}$) directions, respectively [18,20,23]. These dimer rows on the ($10\bar{1}0$) surface consists of chains of Zn and O atoms where each surface Zn(O) atom is bonded to two O(Zn) atoms in the surface layer, and to one O(Zn) atom in the second layer. The ZnO($10\bar{1}0$) surface described above is coincident to what obtaining in our optimized configuration, this surface is thus using for next calculations.

Our calculations for the relaxation of the ($10\bar{1}0$) surface are given in Table 1. The distortion of surface relaxation after structural reconstruction into the bulk is illustrated along with the parameters in Fig. 2(b). In comparison to the topmost surface layer, the tilt angles *θ* of distortion and the in-plane bond-length contraction (Δ*d*) of the Zn—O dimers are smaller in the second and the subsequent layers, but still small deviations from the bulk structure can be seen as deep as six layers below the surface. Calculated tilt angles *θ* and distance *d* of the surface Zn—O bond (see in Fig. 2(b)), an indicator of surface, are 10.13° and 1.87 Å, respectively. These changes are caused by relaxation for ($10\bar{1}0$) face after