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Thermochemistry and micro-kinetic analysis of methanol synthesis on ZnO (0001)

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ABSTRACT

In this work, we examine the thermochemistry of methanol synthesis intermediates using density functional theory (DFT) and analyze the methanol synthesis reaction network using a steady-state micro-kinetic model. The energetics for methanol synthesis over Zn-terminated ZnO (0001) are obtained from DFT calculations using the RPBE and BEEF-vdW functionals. The energies obtained from the two functionals are compared and it is determined that the BEEF-vdW functional is more appropriate for the reaction. The BEEF-vdW energetics are used to construct surface phase diagrams as a function of CO, H_2O, and H_2 chemical potentials. The computed binding energies along with activation barriers from literature are used as inputs for a mean-field micro-kinetic model for methanol synthesis including the CO and CO_2 hydrogenation routes and the water–gas shift reaction. The kinetic model is used to investigate the methanol synthesis rate as a function of temperature and pressure. The results show qualitative agreement with experiment and yield information on the optimal working conditions of ZnO catalysts.

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1. Introduction

The catalytic synthesis of methanol from synthesis gas is one of the most important industrial chemical processes with a worldwide production capacity of around 40 million tons per year [1]. Currently, methanol is used primarily as a starting material or solvent for chemical synthesis, although increasingly, it is employed as a fuel [1–3]. The diversity of compounds that can be synthesized from methanol along with its promise as an energy carrier makes the development of more efficient and sustainable production schemes a priority for the chemical industry of the future [3].

Methanol was originally produced from synthesis gas using a zinc oxide (ZnO) catalyst discovered in the 1920s. The catalyst required high temperatures (600–700 K) and pressures (200–300 bar) to operate industrially [1,2,4]. The high pressure methanol process was rendered obsolete in the 1960s with the development of a lower pressure process based on a Cu–ZnO catalyst [2,4,5]. The active phase of this Cu–ZnO system has been the subject of much debate [1,5–10], though several investigations have shown strong evidence that the active site is on Cu and that the reaction is structure sensitive [10–13].

A detailed understanding of the methanol synthesis reaction is hindered by several fundamental obstacles. The industrial process is carried out at very high pressures which are required to drive the reaction thermodynamics. This presents a challenge in extrapolation of the results of ultra-high vacuum (UHV) studies to relevant conditions. In addition, the elementary steps in methanol synthesis form a complex network due to the possibility of hydrogenating carbon monoxide (CO) or carbon dioxide (CO_2), along with the water–gas shift reaction, which couples the two pathways together. This makes it challenging to elucidate the reaction mechanism, although convincing evidence has been shown for CO hydrogenation on ZnO [14] and for CO_2 hydrogenation on Cu–ZnO [1,5,15]. Furthermore, the industrial Cu–ZnO catalyst exhibits a highly heterogeneous morphology and the activity is dependent on preparation procedures [5,10]. For this reason, it can be difficult to glean understanding from the simplified model systems commonly used in experiment and theory.

In this work, we seek to make progress toward understanding methanol synthesis by investigating the reaction on the ZnO catalyst. The thermochemistry of oxygen and CO adsorption on several ZnO faces is examined, confirming the polar surfaces as the most likely active facets. The interaction of methanol synthesis intermediates with the Zn-terminated ZnO (0001) surface is examined in detail using density functional theory (DFT). These results are used

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to construct a surface phase diagram as a function of CO, H_2O and H_2 chemical potentials. The phase diagram indicates that surface terminations including formate and methoxy are highly stable even at low CO pressures, revealing the importance of considering a carbon reservoir. The energetics are also used in a mean-field micro-kinetic model which includes CO and CO_2 hydrogenation pathways as well as the water–gas shift reaction. This model is employed in order to examine the temperature and pressure dependence of the methanol synthesis rate on ZnO. The results indicate that this model is capable of describing the experimental trends in the operating conditions of the ZnO catalyst and suggest site poisoning by formate (HCOO) as the reason that high temperatures, high total pressures, and low CO_2 concentrations are required.

2. Methods

2.1. Density functional theory

All electronic structure calculations are carried out using the grid-based projector augmented wave code GPAW [16]. Exchange–correlation energies are treated using both the RPBE [17] and BEEF-vdW [18] functionals. All calculations are preformed on a finite-difference grid, and the Brillouin zone is sampled by a Monkhorst–Pack k-point mesh [19]. Several surface facets and system sizes are investigated, and the values of the grid spacing and k-point density required for convergence varied; all systems with their parameters are shown in Table 1. These parameters are determined by converging the CO adsorption energy to within 0.03 eV.

All surfaces are treated in the slab approach with 12 Å of vacuum above and below the slab. The number of layers is determined by converging the adsorption energy of CO to within 0.03 eV, and the upper half of the layers are allowed to relax while the lower half are constrained to their bulk positions. The slabs are treated as non-periodic in the direction perpendicular to the surface (density goes to zero at the boundary), and a dipole correction is applied [20]. The reverse side of the polar (0001) surface is truncated with 0.5 ML of hydrogen atoms in order to prevent an unphysical transfer of electrons to the adsorbate [21,22]. This approach has been used previously [23] and the adsorption energies are within 0.02 eV of those obtained with pseudo-hydrogens. Geometry optimizations are conducted with a quasi-Newton algorithm as implemented in the Atomic Simulation Environment (ASE) [24] until the maximum force is less than 0.05 eV/Å. Global minima are obtained by using initial guesses similar to previous work [25,26]; when this is not possible, the adsorbate is placed on several different high-symmetry sites as an initial guess and the minimum energy site is taken. Geometries can be found in the Supplementary information Section S1.

The energies of surface intermediates are reported as formation energies calculated as follows:

$$E_f = E_{slab+ads} - E_{slab} - \sum_{i \in \{C,H,O\}} n_i \mu_i \tag{1}$$

where $E_{slab+ads}$ is the raw DFT energy of the surface and adsorbate, E_{slab} is the raw DFT energy of the surface slab, n_i is the number of atoms of species i in the adsorbate, and μ_i are reference energies. In this case, the reference energies are given by electronic potential energies (as opposed to Gibbs free energies) and are computed by the following:

$$\begin{aligned} \mu_O &= E_{H_2O} - E_{H_2} \\ \mu_C &= E_{CO} - \mu_O \\ \mu_H &= \frac{1}{4}(E_{CH_3OH} - \mu_C - \mu_O) \end{aligned} \tag{2}$$

where E_j is the DFT gas-phase energy of species j. These references are chosen since gas-phase CO_2 and H_2 calculated with the BEEF-vdW functional need to be corrected in order to obtain reasonable gas-phase reaction energies [27]. Physisorbed and gas-phase CO_2 and HCOOH are corrected to account for the O=C=O error based on thorough statistical analyses of gas-phase energetics as reported previously [27,28].

The transition-state energies for H—CH_2O, CH_3O—H, and OCH_2—OH were calculated using the climbing image nudged elastic band (NEB) method since a degree of rate control analysis indicated that these were the most important transition-states in methanol synthesis (see Figs. 7 and 8). Transition-state energies of most other reactions were taken from literature values when available. The transition-state energies for HCOO—H, H—HCOOH, OCH_2O—H, and O—H were not available in the literature [25,26,29] and were thus estimated using Brønsted–Evans–Polanyi (BEP) scaling [30]. A least-squared fit between the BEEF-vdW reaction energies and the activation barriers in Table 3 indicated that the relationship $E_a \approx 0.34\Delta E_{rxn} + 0.55$ (where E_a and ΔE_{rxn} are the activation and reaction energy of an elementary step) is able to predict hydrogenation barriers with reasonable accuracy (mean absolute error of 0.24 eV). Details are provided in the Supplementary information Section S2. By examining the free energy diagram in Fig. 5 it can be seen that the reaction barriers estimated with BEP scaling are not likely to be rate-limiting, so the accuracy of the scaling is sufficient for the kinetic model. The numerical values and origin of all barriers can be found in Table 3.

Vibrational frequencies are calculated with a normal mode analysis by using a finite-difference approximation of the Hessian matrix as implemented in ASE [24]. The finite-difference delta is 0.01 Å and 4 displacements per Cartesian coordinate. Imaginary frequencies are assumed to correspond to very low vibrational modes and are replaced by 6.8 meV due to the fact that the entropy associated with a mode diverges as the mode goes to zero. The cut-off of 6.8 meV corresponds to an entropy of ca. $3k_B$ at 600 K; it is assumed that below this frequency the entropy would be bounded by other effects.

2.2. Micro-kinetic modeling

The kinetic model is based on assumptions and formalisms described previously [31] and was solved using an automated

Table 1
Parameters used for DFT calculations. Values were determined by converging CO adsorption energy to within 0.03 eV. All unit cells were orthorhombic.

Structure	Unit cell	Composition	k-Points	Grid spacing
ZnO bulk	$a \times \sqrt{3}a \times c$	Zn_4O_4	$8 \times 8 \times 8$	0.18
Gas molecules	$20\,Å \times 20\,Å \times 20$	H_2O, CO, CH_3OH, H_2	$1 \times 1 \times 1$	0.18
$ZnO(11\bar{2}0)$	$\sqrt{3}a \times c \times 30\,Å$	$Zn_{10}O_{10}$	$6 \times 4 \times 1$	0.18
$ZnO(10\bar{1}0)$	$a \times c \times 33\,Å$	Zn_8O_8	$6 \times 4 \times 1$	0.18
ZnO (0001)	$a \times \sqrt{3}a \times 38.5\,Å$	Zn_8O_8	$6 \times 4 \times 1$	0.18
ZnO (0001)	$2a \times 2\sqrt{3}a \times 38.5\,Å$	$Zn_{32}O_{32}$	$4 \times 2 \times 1$	0.18

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