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# Density functional theory study of ethanol synthesis from dimethyl ether and syngas over cobalt catalyst

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## ABSTRACT

The reaction mechanism of ethanol synthesis from dimethyl ether (DME) and syngas was studied via density functional theory calculations. Various possible pathways for ethanol formation, and byproduct formations of methanol, acetic acid, methane, carbon dioxide, and water over an active cobalt stepped surface were calculated. The most favorable pathway for ethanol synthesis starts with the dissociation of dimethyl ether to CH<sub>2</sub>, followed by carbon monoxide insertion to form CH<sub>2</sub>CO, and then undergoes successive hydrogenations to give ethanol. CH<sub>3</sub>CHO hydrogenation to CH<sub>3</sub>CHOH becomes the rate-determining step with a reaction barrier of 1.48 eV. DME decomposition and CH<sub>2</sub> carbonylation occur easily with low barriers of 0.61 eV and 0.48 eV, respectively. Carbon monoxide insertion into CH<sub>2</sub> is more facile than into CH<sub>3</sub> and CH. Hydrogenation at the carbon atom occurs prior to the oxygen atom in the order of α-carbon > carbonyl carbon > oxygen. The calculations demonstrate that ethanol synthesis via DME carbonylation and hydrogenation is thermodynamically favored and is kinetically faster than that via syngas direct synthesis. Methane and acetic acid are two dominant competing byproducts.

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## 1. Introduction

Biomass-derived ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) has been recognized as an alternative fuel to traditional fossil fuels since that its raw material, biomass, is renewable and abundant on the earth. The increasing utilization of ethanol as motor fuel will reduce CO<sub>2</sub> emission. Because of the easy and low cost production of syngas via biomass gasification, direct CH<sub>3</sub>CH<sub>2</sub>OH synthesis from syngas (CO + H<sub>2</sub>) has been studied widely [1–4]. Four categories of heterogeneous catalysts have been tested and optimized: modified Fischer–Tropsch synthesis catalysts (cobalt-based or iron-based), modified methanol synthesis catalysts (copper-based), modified molybdenum-based catalysts, and rhodium-based catalysts [4]. However, drawbacks of severe reaction conditions, low one pass CO conversion, and low CH<sub>3</sub>CH<sub>2</sub>OH selectivity has inhibited its industrial application.

Recently, an improved method for CH<sub>3</sub>CH<sub>2</sub>OH synthesis from dimethyl ether (DME) and syngas has been proposed [5–7]. The synthesis involves the simultaneous or stepwise reactions of DME vapor-phase carbonylation and hydrogenation. It is considered a promising technology because of the high reaction activity and the

efficient production of DME and syngas feedstock from renewable biomass. Iglesia and coworkers found that HMOR and HFER catalyzed DME carbonylation to methyl acetate had stable rates and more than 99% selectivity at 423–463 K, and the rate of DME carbonylation was much higher than that of CH<sub>3</sub>OH carbonylation [8,9]. Tsubaki and coworkers reported that DME was converted completely with a CH<sub>3</sub>CH<sub>2</sub>OH selectivity of 48.4% in the one step CH<sub>3</sub>CH<sub>2</sub>OH synthesis from DME, CO, and H<sub>2</sub> over affordable HMOR and Cu/ZnO dual catalysts [5–7,10,11]. Lu et al. used different noble metals (Pt, Pd, and Ru) to impregnate HMOR and to promote the catalytic activity of CH<sub>3</sub>CH<sub>2</sub>OH synthesis from DME and syngas, and they found that the combination of 0.4 wt% Pt/HMOR and Cu/ZnO catalyst presented excellent catalytic performance [12].

We have studied DME carbonylation over metal modified HMOR catalysts (Cu, Ni, Co, Zn and Ag), and found that the catalytic performances of Co, Cu, and Ni modified HMOR were better than the performance of HMOR [13]. The activity of Co was comparable with that of Cu in DME conversion (close to 100%) and methyl acetate selectivity (higher than 99%), which shows the effectiveness of Co for DME carbonylation. Bartek et al. reported that CH<sub>3</sub>CH<sub>2</sub>OH/acetaldehyde (CH<sub>3</sub>CHO) selectivities were promoted significantly when Co based catalysts were used in the reductive carbonylation of DME [14]. Co is highly active for ester and aldehyde hydrogenation to produce alcohols [15–17]. Co catalysts are

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considered as promising candidates for CH<sub>3</sub>CH<sub>2</sub>OH synthesis from DME and syngas via synergic carbonylation and hydrogenation.

In this work, we study the mechanism of CH<sub>3</sub>CH<sub>2</sub>OH synthesis from DME and syngas over a Co catalyst via density functional theory (DFT) calculations. A stepped surface was used in the calculation because it is recognized as the most active site of transition metals for heterogeneous catalytic reactions [18,19]. Adsorptions of key intermediates were firstly calculated to identify their preferred surface adsorption geometries. Then the elementary reactions for DME decomposition, subsequent CO insertion into CH<sub>x</sub> (x = 1–3) and successive hydrogenation to CH<sub>3</sub>CH<sub>2</sub>OH, and the competing reactions of direct CO hydrogenation to CH<sub>3</sub>OH and CH<sub>3</sub>CH<sub>2</sub>OH were calculated. Acetic acid (HOAc), CO<sub>2</sub>, water (H<sub>2</sub>O), and methane (CH<sub>4</sub>) byproduct formations were also considered. Finally, the most likely reaction pathways for CH<sub>3</sub>CH<sub>2</sub>OH, CH<sub>3</sub>OH, HOAc, and CH<sub>4</sub> were identified. To the best of our knowledge, this is the first theoretical study that presents thermodynamic and kinetic reaction barriers of CH<sub>3</sub>CH<sub>2</sub>OH synthesis from DME and syngas.

## 2. Computational Methods

All spin-polarized periodic DFT calculations were carried out using the Vienna Ab initio Simulation Package (VASP) [20–22], and the Perdew–Burke–Ernzerhof (PBE) generalized gradient correction (GGA) was used to treat exchange and correlation effects. The core electrons of all atoms were described by the projector-augmented wave pseudopotential, and the energy cutoff was 400 eV. Monkhorst Pack k-point mesh of 6 × 6 × 6 and 3 × 3 × 1 for bulk and surface calculations were used to sample the Brillouin zone. The Fermi level was smeared using the Methfessel Paxton method with a width of 0.1 eV. The electronic self-consistent field converged to 1 × 10<sup>−4</sup> eV and forces on all atoms converged to less than 0.05 eV/Å.

A fcc Co close-packed unit cell with an original lattice constant of 3.544 Å was selected and optimized by a conjugate-gradient algorithm. The calculated equilibrium bulk lattice constant for Co is 3.524 Å, which agrees well with theoretical (3.521 Å) and experimental values (3.545 Å) [23,24]. Co steps were modeled by using a four layer thick slab of 3 × 3 Co(111) surface supercell, from which two closed packed rows were removed to form a step. The atoms of the bottom two layers were fixed in the bulk positions, whereas the others were allowed to relax to their lowest energy configurations. A vacuum space of 15 Å was applied to avoid the interaction between the slab and its images. The side and top views of the model Co stepped surface are shown in Fig. 1.

The transition states (TS) were determined by the climbing nudged elastic band method (CINEB) [25,26]. This method gives a precise estimate of the saddle point with a small modification of the regular efficient NEB method. It has been widely used for TS searching and the minimum energy path finding [18,23,27–30]. In our calculation, an elastic band with 8 structural images along the path of the initial state (IS) and the final state (FS) of each elementary reaction were constructed by linear interpolation. A spring interaction between adjacent images was added to ensure continuity of the path, and optimized using quick-min algorithm. After being converged, the image with the highest energy (TS) was not affected by the spring forces at all. The TS structures were further confirmed by vibrational frequency analysis and determining that only a single imaginary frequency presented along the proper reaction coordinate. All vibrational frequencies were calculated by allowing the entirety of the adsorbed species on the surface to fully relax while all the Co atoms were kept fixed. The reaction rate constants were calculated using the harmonic transition-state theory.

The adsorption energy  $\Delta E_{\text{ads}}$  is defined as  $\Delta E_{\text{ads}} = E_{\text{ads/slab}} - E_{\text{slab}} - E_{\text{gas}}$ , where  $E_{\text{ads/slab}}$  is the total energy of the slab with

adsorbates,  $E_{\text{slab}}$  is the slab energy, and  $E_{\text{gas}}$  is the energy of adsorbates in the gas phase. The reaction energy ( $\Delta H$ ) and activation energy ( $E_a$ ) are defined as  $\Delta H = E_{\text{FS}} - E_{\text{IS}}$ , and  $E_a = E_{\text{TS}} - E_{\text{IS}}$ , respectively.  $E_{\text{IS}}$ ,  $E_{\text{TS}}$ , and  $E_{\text{FS}}$  are the total energies of the IS, TS, and FS, respectively.

## 3. Results

### 3.1. Adsorptions of Intermediates

Adsorption geometries of some key reaction intermediates on the Co stepped surface are presented in Fig. 2. The corresponding adsorption geometrical parameters, configurations, and adsorption energies are listed in Table 1. The nomenclature  $\eta^i-\mu_j$  was used to designate  $i$  atoms of the adsorbate bound to  $j$  atoms on the metal surface.

Saturated species, dimethyl ether (CH<sub>3</sub>OCH<sub>3</sub>), CH<sub>3</sub>OH, and CH<sub>3</sub>CH<sub>2</sub>OH, have small adsorption energies that range from −0.42 to −0.62 eV, and which demonstrate weak binding to the surface. The adsorptions are induced by the lone pair electrons of O atoms in those adsorbates, forming  $\eta^1-\mu_1(\text{O})$  configurations with an O–<sup>s</sup>Co distance of 2.09–2.14 Å (Figs. 2(a–c)). For CH<sub>3</sub>CHO and HCHO (Fig. 2(d,e)), the adsorption energy increases to −1.42 and −1.59 eV, respectively, and give stronger binding to the surface than that of CH<sub>3</sub>OCH<sub>3</sub>, CH<sub>3</sub>OH, and CH<sub>3</sub>CH<sub>2</sub>OH. This can be ascribed to a relatively strong d–π interactions between the d orbital of <sup>s</sup>Co atoms and the π bond of C=O in CH<sub>3</sub>CHO and HCHO. Both  $\eta^2-\mu_2(\text{C,O})$  configurations were generated with an O atom located at the bridge site and a carbonyl C atom located at the top site of the <sup>s</sup>Co atoms. The O–<sup>s</sup>Co distances are shortened by ~0.15 Å compared with those of CH<sub>3</sub>OCH<sub>3</sub>, CH<sub>3</sub>OH, and CH<sub>3</sub>CH<sub>2</sub>OH species.

Unsaturated species bind strongly to the surface through stepped Co atoms with adsorption energies that range from −2.02 to −4.00 eV, which are larger than the saturated species. The CH<sub>3</sub>OCH species is the most strongly adsorbed intermediates on the surface with binding energy of −4.00 eV. The corresponding configuration is  $\eta^1-\mu_2(\text{C})$ . With the elimination of hydrogen atoms and a decreasing symmetry for CH<sub>3</sub>OCH<sub>3</sub> decomposition intermediates (Figs. 2(a, f–h)), the adsorption sites change from oxygen to carbon atoms and the corresponding adsorption configurations follow  $\eta^1-\mu_1(\text{O}) \rightarrow \eta^2-\mu_2(\text{C,O}) \rightarrow \eta^1-\mu_2(\text{C})$ . The reason may be assigned to the favorable formation of a tetrahedral bonding geometry for carbon atoms on the surface [31].

The adsorption of COH on the surface is strong. The C atom located at the bridge site is linked to two <sup>s</sup>Co atoms on the stepped surface, giving a  $\eta^1-\mu_2(\text{C})$  configuration (Fig. 2(n)). The corresponding adsorption energy is −3.84 eV with  $d_{\text{C}-\text{sCo}}$  of 1.81 and 1.82 Å. The alkoxide species, CH<sub>3</sub>O and CH<sub>3</sub>CH<sub>2</sub>O are also two strong adsorption intermediates, which have the binding energies of −3.55 and −3.52 eV, respectively. The resulting binding configurations are  $\eta^1-\mu_2(\text{O})$  (Figs. 2(i) and (o)). The binding atoms change from carbon to oxygen compared with COH. The length of O–<sup>s</sup>Co bonds for CH<sub>3</sub>O and CH<sub>3</sub>CH<sub>2</sub>O are 1.92 and 1.93 Å, respectively, which are 0.11 Å longer than that for  $d_{\text{C}-\text{sCo}}$  in COH.

Both CH<sub>3</sub>CHOH and CH<sub>2</sub>OH have the adsorption configurations of  $\eta^2-\mu_2(\text{C,O})$  through their unsaturated C atoms and hydroxyl O atoms on the surface, while CHOH is linked to the surface through its C atom only to give a  $\eta^1-\mu_2(\text{C})$  configuration. The calculated configurations are in good agreement with the previous DFT results [29,32]. It can be ascribed to that with the increase of the valence saturation of C atom (the maximum is 4) in adsorbates, the adsorption induced by C atom becomes weaker and weaker, while that induced by O atom becomes dominant. The O and unsaturated C atoms are competitive adsorption on the surface, with C being pre-

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