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Methanol synthesis from CO_2 hydrogenation over a Pd_4/In_2O_3 model catalyst: A combined DFT and kinetic study

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ABSTRACT

Methanol synthesis from CO_2 hydrogenation on a model Pd/In_2O_3 catalyst, i.e. Pd_4/In_2O_3, has been investigated using density functional theory (DFT) and microkinetic modeling. Three possible routes in the reaction network of $CO_2 + H_2 \rightarrow CH_3OH + H_2O$ have been examined. Our DFT results show that the HCOO route competes with the RWGS route whereas a high activation barrier blocked the HCOOH route kinetically. The DFT results also suggest that $H_2COO^* + H^* \leftrightarrow H_2CO^* + OH^*$ and cis-$COOH^* + H^* \leftrightarrow CO^* + H_2O^*$ are the rate-limiting steps in the HCOO route and the RWGS route, respectively. Microkinetic modeling results demonstrate that the HCOO route is the dominant pathway for forming methanol from CO_2 hydrogenation. Furthermore, the activation of the H adatom on the Pd cluster and the presence of H_2O on the In_2O_3 substrate play important roles in promoting methanol production. The hydroxyl adsorbed at the interface of Pd_4/In_2O_3 induces structural transformation of the supported Pd_4 cluster from a butterfly shape into a tetrahedron one. This structural change not only indicates the dynamical nature of the supported nanocatalysts during the reaction but also causes the final hydrogenation step to change from CH_3O to H_2COH.

1. Introduction

Hydrogenation of CO_2 into methanol has attracted attention worldwide for its role in chemical sequestration of CO_2 [1–4]. Many catalysts have been exploited for this reaction and among them, supported Pd catalysts including Pd/Ga_2O_3 [5], Pd/CeO_2 [6], Pd/ZnO [7] and Pd/ZrO_2 [8] have shown high activity. For supported Pd catalysts, the supports and promoters (mostly metal oxides) play important roles in the activity and selectivity for methanol production. For example, the effect of metal oxide supports has been found to follow the order of $Ga_2O_3 > ZnO > Al_2O_3 > TiO_2 \approx Cr_2O_3 > SiO_2 \approx ZrO_2$ [5]. Bonivardi et al. showed that the addition of Ga_2O_3 into a Pd/SiO_2 catalyst increases the turnover rate by 500-fold and the selectivity toward methanol to 70% from 17% as compared with those on the clean Pd/SiO_2 [9]. Iwasa and coworkers suggested that the remarkable activity and selectivity of Pd/Ga_2O_3 catalysts for either methanol synthesis or for the methanol stream reforming were a consequence of Pd–Ga alloy formation [10,11]. The roles of metal oxides are summarized as: (1) the metal oxides help to disperse and stabilize the Pd particles or form bi-metallic particles due to their strong interactions with Pd; (2) the metal oxides (basic or amphoteric) generally have a higher affinity toward CO_2, and are thereby beneficial for CO_2 adsorption and activation; (3) the carbon monoxide ascribed to the reverse water–gas shift (RWGS) mainly proceeds on the metal oxides since Pd has a low activity for the RWGS reaction [5].

In_2O_3 has been well known for its unique physical properties of optical transparency and electrical conductivity [12–16]. However, the interesting catalytic properties of In_2O_3 have not attracted much attention until recently [17–22]. The Pd/In_2O_3 catalyst showed high selectivity for CO_2, and correspondingly low CO productivity, in the methanol steam reforming (MSR) for hydrogen production and this was attributed to formation of the Pd–In alloy at low temperatures [10,22–27]. Iwasa et al. reported that methanol can be produced from CO_2 as a feed gas with H_2 on Pd/In_2O_3, but not from CO [28]. Since methanol steam reforming is the reversal of methanol synthesis from CO_2 hydrogenation, methanol formation from CO_2 hydrogenation on Pd/In_2O_3 is expected to go through the direct hydrogenation of CO_2.

The interfacial sites are unique to the supported metal catalyst and play an important role in heterogeneous catalysis. The synergetic effect of H_2 dissociation on Pd particles and the spillover of

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the H adatoms to the support where CO_2 is adsorbed play important roles for methanol synthesis from CO_2 hydrogenation [29–31]. Very recently, Kwak et al. demonstrated that atomically dispersed Pd assisted by oxides, either as support (Al_2O_3) or promoter (La_2O_3), exhibits activity toward CO_2 reduction whereas Pd supported on a carbon nanotube support without oxide does not [32]. In fact, atomically dispersed supported metal catalysts have become an intensely focused area of research in recent years [33–37]. H_2 adsorption and dissociation on the pure Pd surfaces or particles have been studied both experimentally [31,38] and theoretically [39–41]. The interaction of H_2 and Pd is closely related to the H_2 pressure and particle size of Pd. The strong interaction between H atoms and the small Pd particles (Pd_n, $n = 3, 4$) results in incorporation of the H atoms into the Pd cluster [40], which strongly suppresses the activity of H for CO_2 hydrogenation. Consequently, activation of the strongly bound H atoms needs to be taken into account in CO_2 hydrogenation, especially on a supported Pd nanoparticle. In addition, the dissociation of H_2, H_2O and other intermediates (i.e. COOH, HCOOH, H_2COOH) produces a large amount of hydroxyls during the reaction, which are likely to adsorb on the In_2O_3 surface [18,20,21]. As a result, the effect of hydroxyls on the reaction mechanism has also to be examined carefully. For example, studies of CO_2 hydrogenation on Ni_4/γ-Al_2O_3 [42] indicate that the hydroxyls on the γ-Al_2O_3 support alter the reaction pathway for CO_2 hydrogenation and ultimately affect the distribution of the final products.

Previously, theoretical studies of methanol synthesis from CO_2 were carried out on a pure metal surface (Cu(1 1 1) [43–45]), a metal cluster (Cu_{29} [44]), a metal doped Cu surface [46] or a bare metal oxide (ZnO [47]). On the supported metal catalysts, the adsorption and dissociation of H_2 usually occur on the surface of the metal particle. Murray et al. found that carbon monoxide oxidation in ceria-based catalysts is greatly enhanced at the ceria–metal interface sites for a range of group VIII metal catalysts [48]. Heiz et al. reported that a single Pd atom supported on MgO is active for the production of benzene, but a free Pd atom is inert for this reaction [49]. The activity of Pd/MgO was attributed to the charge transfer from the support to the metal cluster as revealed by the DFT study. In fact, models such as Pd_n/MgO [49] and Ni_4/γ-Al_2O_3 [42] become attractive model systems. These simplified model systems capture key features of the metal–support interaction and provide interfacial sites as active sites for the catalytic transformation whereas quantitative agreement with the experimental system is generally not anticipated. Since CO_2 generally physisorbs on metallic Pd [50–52], the hydrogenation of CO_2 likely utilizes hydrogen adatoms generated on Pd and proceeds at the interface of the metal particle and the support. Herein, a Pd_4 cluster supported on In_2O_3 (Pd_4/In_2O_3) was designed as a model catalyst to elucidate the mechanism of methanol synthesis from CO_2 hydrogenation using a combination of density functional theory calculation and microkinetic study. The effects of H adatom activation, water and hydroxyl on the reaction mechanism and kinetics were also examined. The results confirmed that Pd on In_2O_3 would be a good catalyst for methanol synthesis from CO_2 hydrogenation.

2. Methodology and models

All the calculations were performed using the Vienna ab initio simulation package (VASP) [53–55], a periodic DFT code with projector augmented wave (PAW) potentials. The nonlocal exchange correlation energy was evaluated using the Perdew–Burke–Ernzerhof functional [56]. The 5s and 5p states of In were treated explicitly as valence states within the scalar-relativistic PAW approach [57]. A plane wave basis set with a cutoff energy of 400 eV and a $(2 \times 2 \times 1)$ k-point grid generated with the Monkhorst–Pack scheme were found to give converged results. The atomic structures were relaxed using either the conjugate gradient algorithm or the quasi-Newton scheme as implemented in the VASP code until the forces on all unconstrained atoms were less than 0.03 eV/Å.

The $In_2O_3(1\,1\,0)$ surface is modeled with a $(1 \times \sqrt{2})$ supercell, built from the optimized In_2O_3 bulk unit cell with lattice parameters $a = b = c = 10.18$ Å [19,20]. The supercell has a dimension of 10.18 Å × 14.40 Å × 17.96 Å. The surface slab consists of 48 O atoms and 32 In atoms distributed in four atomic layers and is separated by a vacuum of 12 Å. The optimized Pd_4 cluster with a tetrahedral structure is supported on the $In_2O_3(1\,1\,0)$ surface to generate the Pd_4/In_2O_3 model catalyst. In all calculations, atoms in the bottom two layers of the $In_2O_3(1\,1\,0)$ slab are frozen at their equilibrium bulk positions whereas those in the top two layers together with the Pd_4 cluster and other species involved in methanol synthesis are allowed to relax. Test calculations by increasing the vacuum space to 15 Å showed that the adsorption energy of CH_3OH is −0.78 eV, almost exactly the same as that from the slab with 12 Å vacuum. The reaction energy and activation barrier for bi-$HCOO^* + H^* \rightarrow H_2COO^* + *$, an elementary step in methanol formation, are +0.77 eV and 1.10 eV, respectively, also very close to those (+0.75 eV and 1.09 eV, respectively) from the slab with 12 Å vacuum.

The adsorption energies of intermediates were defined as:

$$\Delta E_{ad}(M) = E_{M/(Pd_4/In_2O_3)} - E_{(Pd_4/In_2O_3)} - E_{(M)}$$

where M represents molecules, intermediates involved in methanol synthesis as well as their corresponding products upon adsorption. $E_{M/(Pd_4/In_2O_3)}$, $E_{(Pd_4/In_2O_3)}$ and $E_{(M)}$ represent the total energies of the Pd_4/In_2O_3 with the adsorbate and the clean Pd_4/In_2O_3, the free molecule or intermediate, respectively. In the case of co-adsorption and reaction on the surface, the relative energies were computed with respect to the sum of the total energies of the corresponding free molecules. According to the above definition, negative values indicate that the process is exothermic whereas positive values indicate that the process is endothermic. Transition states along a reaction pathway were determined in two steps: First, the nudged elastic band method [58], typically with 7–9 images was used to locate the likely transition state; second, the likely transition state was relaxed using the quasi-Newton algorithm with the same force convergence criterion. The relaxed transition state was then confirmed through frequency analysis.

3. Results and discussion

3.1. Pd_4 supported on $In_2O_3(1\,1\,0)$

The side and top views of $In_2O_3(1\,1\,0)$ and $Pd_4/In_2O_3(1\,1\,0)$ are shown in Fig. 1. The structure of $In_2O_3(1\,1\,0)$ has been discussed in our previous papers in detail [19,20]. In the present study, we focus on $Pd_4/In_2O_3(1\,1\,0)$. The optimized Pd_4 cluster is a tetrahedron in the gas phase [59]. The initial $Pd_4/In_2O_3(1\,1\,0)$ structure was built by placing the optimized Pd_4 cluster on the $In_2O_3(1\,1\,0)$ surface. After relaxation, the Pd_4 cluster is stabilized on the surface by bridging between the two In–O chains through the Pd–In and the Pd–O bonds (Pd_1–In_2: 2.62 Å, Pd_3–In_4': 2.78 Å, Pd_4–O_2: 2.16 Å, Pd_4–O_4': 2.13 Å, Pd_2–O_3: 2.11 Å, Pd_2–O_5': 2.11 Å). We note that the original tetrahedral structure of Pd_4 was distorted into a butterfly shape after optimization. The average Pd–Pd bond length is shortened from 2.61 Å in a Pd_4 tetrahedron to 2.56 Å. The angles of $\angle Pd_{1\text{-}4\text{-}3}$ and $\angle Pd_{1\text{-}2\text{-}3}$ are opened from 60° to ~85.0°, whereas the dihedral angle between the $Pd_{1\text{-}2\text{-}4}$ plane and the $Pd_{3\text{-}2\text{-}4}$ plane is opened from 70.5° to 105.6°. The $Pd_4/In_2O_3(1\,1\,0)$ structure is