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First-principles study of the methyl formate pathway of methanol steam reforming on PdZn(1 1 1) with comparison to Cu(1 1 1)

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ABSTRACT

Methanol steam reforming (MSR), catalyzed by the PdZn alloy, produces hydrogen gas and carbon dioxide with high selectivity. However, the mechanism for MSR has not been completely elucidated. It has been proposed that formate and methyl formate are possible intermediates in MSR. In this study, plane-wave density functional theory was used to investigate the role of methyl formate in MSR on PdZn. It is shown that methyl formate can indeed be formed by a reaction between formaldehyde and methoxyl. In the presence of surface OH species, methyl formate can further react to form formic acid, which can finally dehydrogenate to produce CO_2. However, our calculations show that this hydrolysis process might have difficulties competing with desorption of methyl formate, which is weakly adsorbed on the PdZn surface. Our calculated results thus suggest a minor role for the methyl formate pathway in MSR. Interestingly, the methyl formate reaction pathway shares many similarities with the same process on copper, which is the traditional catalyst for MSR. The insights gained by studying the reaction mechanism on these two surfaces shed valuable light on designing future catalysts for the MSR process.

1. Introduction

Hydrogen based proton exchange membrane (PEM) fuel cells provide a highly efficient and environmentally friendly solution to future transportation and mobile power needs of the post-model society, but their popularization has been fraught with difficulties, partly because of the unsolved problem of hydrogen storage and transportation. A possible solution is to generate hydrogen on board and on demand, using, for example, methanol steam reforming (MSR) [1–3]:

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad \Delta H^\circ = 49.6\,\text{kJ/mol}.$$

The use of methanol as a hydrogen carrier has a number of advantages [4]. First, it is a liquid fuel which can be readily stored and transported using the infrastructure for the existing transportation fuels with minor modifications. Second, the technology for large scale production of methanol from other feedstocks, including CO_2, is well established and industrial capacity exists. Finally, it is a relatively clean fuel, with a high H/C ratio and no sulfur or nitrogen; and it is miscible with water and biodegradable.

MSR can be realized with a number of catalysts [1,2]. The traditional catalyst is copper dispersed on oxide support. This catalyst has high selectivity toward CO_2, producing only a very small amount of CO. This is important because anodes of PEM fuel cells do not tolerate CO very well. However, the copper catalyst has a few undesirable features, including low thermal stability due to metal sintering and pyrophoricity. For these reasons, there is a strong desire for more stable and equally active and selective MSR catalysts. A recently discovered alternative catalyst of MSR, PdZn, has been shown to have much better thermal stability while maintains the high efficiency and selectivity [5–10]. This discovery has stimulated many recent research activities on the new catalyst [11–17]. There have been some suggestions that the two catalysts have similar electronic properties and might share the same catalytic mechanism [18–20]. However, detailed evidence is still sketchy.

A better understanding of the catalytic mechanism of MSR is important for the design of new and more efficient catalysts. To this end, several reaction pathways have been proposed [7,21]. All these proposed mechanisms assume that MSR is initiated by O—H bond cleavage in both methanol and water, producing adsorbed methoxyl (CH_3O^*) and hydroxyl (OH^*) species, respectively. The catalysis is limited by the dehydrogenation of chemisorbed methoxyl to formaldehyde (CH_2O^*), an assumption supported by both experimental [22–25] and theoretical evidence [26–33]. The surface formaldehyde is known to be a key intermediate in MSR

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[7,9,34], and its further transformations branch out to various other intermediates and products. Several recent theoretical studies have revealed that the reaction of formaldehyde with hydroxyl species on both Cu and PdZn surfaces dominates over the desorption and other reaction channels [33,35,36], including the one that leads to the CO production via the dehydrogenation of formaldehyde [26,27]. The subsequent steps result in various intermediates, such as formate (CHOO*), formic acid (CHOOH*) and dioxomethylene (CH_2OO^{**}), and eventually the production of CO_2 and H_2. Based on these theoretical results, it is now recognized that the reaction between formaldehyde and hydroxyl, while not rate limiting, is the key for the observed selectivity with both Cu and PdZn [33,35]. In addition, our recent DFT studies have demonstrated that the subsequent steps initiated by this reaction are indeed quite similar on the Cu and PdZn surfaces [36].

An alternative MSR pathway involving methyl formate ($CHOOCH_3$) has been proposed by several authors [21,23,34,22], based on the observation that this molecule has been found to desorb from Cu and PdZn surfaces if insufficient steam is provided [7,37,38]. It was also reported that the steam reforming of methyl formate also produces the same CO_2 product as in MSR, even with higher rate [37]. However, the intermediacy of methyl formate in MSR is not supported by diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) experiments by Peppley et al. [23] and more recently by Frank et al. [21], who found no methyl formate on the surface of copper catalysts under normal MSR conditions. Interestingly, the latter did detect signatures of methoxyl, hydroxyl, and formate, which support the formate mechanism discussed above. To resolve this controversy, we have recently shown using plane-wave density functional theory (DFT) that the methyl formate pathway is of minor importance in MSR on Cu, because the reaction of methyl formate with hydroxide cannot compete with that between formaldehyde and hydroxyl [39]. In the current work, we explore this pathway on a PdZn surface using the same plane-wave DFT method [40]. As our results suggest, the reaction steps on PdZn(1 1 1) are similar to those on Cu(1 1 1) and we thus conclude that the methyl formate species are not extensively involved in MSR on PdZn catalyst either.

2. Theory

The PdZn catalyst is modeled in this work by a slab of 1:1 PdZn alloy. This is a reasonable approximation as the PdZn alloy has been identified as the active phase of the catalysis. We will focus here on the (1 1 1) face of the crystal, which is known to be the most stable among various crystal faces of PdZn [18]. Like in our previous work [32,35], all calculations were carried out based on the periodic DFT calculations by using the Vienna ab initio simulation package (VASP) [41–43] with the gradient-corrected PW91 exchange-correction functional [44]. For valence electrons a plane-wave basis set was employed with a cut-off of 400 eV and the ionic cores were described with the projector augmented-wave (PAW) method [45,46]. A $3 \times 3 \times 1$ Monkhorst–Pack *k*-point grid was adopted to sample the Brillouin zone [47], which was tested to be sufficiently accurate for all the calculations. The Fermi level was smeared using the Methfessel–Paxton method with a width of 0.1 eV [48].

Bulk crystal optimization yielded lattice parameter of $a = b = 4.139$ Å, $c = 3.378$ Å for PdZn, in good agreement with the previously reported results [18]. Slab model for the PdZn(1 1 1) surface consisted of four layers of a 4×4 unit cell with the top layer relaxed in all calculations. A vacuum spacing of 14 Å was used and all adsorbates were placed on one side of the slab.

The adsorption energy was calculated as follows: $E_{ads} = E(\text{adsorbate} + \text{surface}) - E(\text{free molecule}) - E(\text{free surface})$. The climbing image nudged elastic band (CI-NEB) method [49,50] was used to determine the transition states with the conventional energy (10^{-4} eV) and force (0.05 eV/Å) convergence criteria. Stationary points were confirmed by normal mode analysis using a displacement of 0.02 Å and an energy convergence criterion of 10^{-6} eV; and the vibrational frequencies were used to compute zero-point energy (ZPE) corrections.

3. Results

3.1. Adsorption

Since many surface species involved in the initial steps of MSR have already been investigated on PdZn(1 1 1) using the plane-wave DFT method [27,28,32,36], we here only focus on the pertinent species in latter steps. The adsorption energies and geometries of the preferred adsorption configurations for several key species are listed in Table 1.

Our calculations indicate that methyl formate adsorbs above the Pd_2Zn_2 parallelogram with its carbonyl oxygen on the top of Zn atom. In addition, two of the hydrogens in the methyl group are pointing to two Pd atoms. This adsorption pattern is consistent with previous theoretical findings that the electronegative oxygen species prefers the zinc site. This closed-shell species has a small adsorption energy of −0.13 eV on PdZn(1 1 1), similar to that found on Cu(1 1 1) [39,51]. Note that DFT is not known to give accurate description of dispersion forces, so the calculated adsorption energy should not be considered to be quantitatively accurate.

The unsaturated species in Table 1 all bind to the PdZn surface with much larger adsorption energies. Unlike the homogenous Cu surface, the heterogeneous PdZn surface offers two distinct active sites. Generally, the electron rich oxygen moiety has a preference on the zinc site while the electron poor carbon and hydrogen moieties prefer to stick to Pd sites. For example, CH_3^* preferentially adsorbs on the top of Pd through its carbon atom. The distance between the C atom and surface Pd atom is 2.14 Å. The binding energy was found to be −1.40 eV, which is very close to that on Cu (−1.42 eV). Similar to Cu(1 1 1), the $CH_2OOCH_3^*$ species adsorbs on PdZn(1 1 1) with its carbonyl oxygen at an $PdZn_2$ hollow site with methyl pointing away from the surface as shown in Table 1. Its adsorption energy of −2.07 eV is also close to the value of −2.03 eV on Cu. The distances between the adsorbing O atom and the two surface Zn atoms are 2.07 Å, while the length of Pd—O is about 2.39 Å. The C—O—C and O—C—O angles were found to be 114.65° and 112.42°, respectively.

An intermediate species from the dehydrogenation of $CHOOCH_3^*$, namely, $CHOOCH_2^{**}$, adsorbs with its methylene carbon and carbonyl oxygen on the top of Pd and Zn atoms, respectively. The adsorption energy of this species is −1.31 eV, which is somewhat larger than that on Cu (−0.84 eV). Finally, the reaction of OH* and $CHOOCH_3^*$ leads to the generation of the $CHOOHOCH_3^{**}$ species. Similar to Cu(1 1 1), $CHOOHOCH_3^{**}$ also has two possible adsorption configurations on PdZn(1 1 1), namely, $CHOOHOCH_3(I)^{**}$ and $CHOOHOCH_3(II)^{**}$. The former species adsorbs through the hydroxyl oxygen on the top of a Pd atom and another carboxylate oxygen atom at the Zn–Zn short bridge site, as shown in Table 1. The distance between hydroxyl oxygen and Pd atom is found to be 2.50 Å and the lengths of Zn—O (bridge site) are 2.08 and 2.10 Å, respectively. The three O—C—O angles are calculated to be 110.75°, 104.75° and 112.79°, respectively, which is almost equal to those on Cu (110.61°, 104.16° and 113.46°) and the C—O—C angle turns to be 114.33°, slightly larger than the value of 113.42° on Cu. Different from $CHOOHOCH_3(I)^{**}$, $CHOOHOCH_3(II)^{**}$ interacts with PdZn(1 1 1) surface through methoxyl O on the top of Pd atom and a carboxylate oxygen at the short Zn–Zn bridge site. Furthermore, the three O—C—O angles become to be 113.51°,