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Article

First-principle insights into the catalytic role of indium oxide in methanol steam reforming

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ABSTRACT

Using first-principle methods, we have shown that formaldehyde can be selectively converted to CO₂ over In₂O₃(110). The OH generated from the splitting of water was found to assist in the dehydrogenation of formaldehyde to give the corresponding formyl (CHO) species. Rather than direct dehydrogenation, a hydrogen atom from the CHO was then removed by a neighboring OH to produce CO. Finally, in favoring of desorption, the CO seized a lattice O atom to yield CO₂. Our calculation results indicate that In₂O₃ plays an important role in terms of selectivity during the methanol steam reforming reaction without the participation of the PdIn alloy, confirming the experimentally observed selectivity towards CO₂.

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1. Introduction

Although hydrogen based proton exchange membrane (PEM) fuel cells represent an efficient and environmentally friendly solution to the growing transportation and mobile power needs of the world, their application in this regard have been limited partly because of the problem associated with the storage and transportation of hydrogen. Fortunately, methanol steam reforming (MSR) provides an effective solution to this problem for the generation of hydrogen [1,2], with the process occurring as follows:

There are several key advantages to an MSR-based solution, including: (1) the system derives hydrogen from a liquid fuel, which can be safely stored and transported; (2) the technology for the large scale production of methanol from other feedstocks is well established, with significant industrial capacity already in place; and (3) with its high H/C ratio and the ab-

sence of sulfur or nitrogen, MSR can be considered as a clean fuel [3].

A large number of mechanistic studies have been conducted on transition metal catalyzed MSR processes using metals such as Cu and Pd supported on ZnO, because of the industrial importance of the MSR process [1,2,4–15]. Catalysts of this particular type have been shown to possess high levels of selectivity towards CO₂ over CO, which is important for potential fuel cell applications because the formation of a CO byproduct would otherwise poison the anodes of PEM fuel cells [1,2]. The synthesis of a new catalyst consisting Pd supported on In₂O₃ was recently reported by Iwasa et al. [5] who also found that the material exhibited extremely high levels of catalytic activity towards the MSR process. In a similar manner to PdZn, the bimetallic PdIn alloy resulting from the heating of Pd and In₂O₃ under reductive conditions is believed to be beneficial for switching from CO-selective methanol dehydrogenation to CO₂ selective MSR. A subsequent experiment revealed that the use

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of In_2O_3 in isolation as a catalyst for the MSR reaction did not provide high levels of CO_2 selectivity [16]. The behavior of pure In_2O_3 in the MSR reaction is therefore very similar to that of pure ZnO , which provides similar levels of CO_2 selectivity (95%–99.6%), albeit with low specific activity as well as an oxide component that has been speculated to enhance the selective conversion of formaldehyde-containing species [17,18]. Interestingly, the results of an experiment recently conducted by Bielz et al. [19] indicated that the use of formaldehyde as a reagent led to 95% selectivity towards CO_2 on a pure In_2O_3 catalyst under typical steam reforming conditions. In contrast, Klötzer et al. [20] recently demonstrated that formaldehyde was only partially converted to CO_2 using a PdIn phase, and that a high CO_2 turnover frequency value could only be obtained when the reaction temperature was increased to at least 593 K. Although these findings did not definitively confirm the role of In_2O_3 in the MSR process, they provided the suggestion that In_2O_3 plays a critical role in the transformation of formaldehyde to CO_2 . From a theoretical perspective, Ge et al. [21] reported that it was unlikely that the dehydrogenation of methanol to CO occurred on the $\text{PdIn}(110)$ surface because of the high energy barriers.

To our best knowledge, very few theoretical studies have been published pertaining to the mechanistic aspects of this particular system because of the complex structure of In_2O_3 [22–26]. Lin et al. [22] recently reported that methanol and water could both be dehydrogenated to form formaldehyde and hydroxyl intermediates, respectively. Herein, to develop a better understand of the catalytic role of In_2O_3 in the MSR reaction, we have conducted for the first time a periodic density functional theory (DFT) study for the selective conversion of formaldehyde to CO_2 .

2. Theory

All of the calculations carried out in the current study were based on periodic DFT calculations using the Vienna ab initio simulation package (VASP) [27–29] with the gradient-corrected PW91 exchange-correction functional [30]. A plane-wave basis set was employed for the valence electrons with a cut-off of 500 eV, and the ionic cores were described according to the projector augmented-wave (PAW) method [31,32]. A $2 \times 2 \times 1$ Monkhorst-Pack k -point grid was adopted to sample the Brillouin zone, which was tested as being converged. The lattice parameter of In_2O_3 was calculated to be 10.328 Å, which was in good agreement with the previously reported results [22,26]. The $\text{In}_2\text{O}_3(110)$ surface was selected as a slab model, consisting of four atomic layers of a 1×1 unit cell with all eighty atoms in the top two layers being completely relaxed in all of the calculations. A vacuum spacing of 14 Å was used to avoid any interactions between the adsorbates and the slab images in the z direction.

The adsorption energy was calculated using the formula $E_{\text{ads}} = E(\text{adsorbate} + \text{surface}) - E(\text{free molecule}) - E(\text{free surface})$. The climbing image nudged elastic band (CI-NEB) method [33] was used to determine the transition states with the conventional energy (10^{-4} eV) and force (0.03 eV/Å) convergence cri-

teria. The highest image along the minimum energy path was denoted as the transition state. The energy barrier E_a of each elementary reaction was calculated from the energy difference between the transition state and the initial state. The reaction energy ΔE of each elementary reaction was calculated from the energy difference between the final state and the initial state.

3. Results and discussion

3.1. Adsorption of pertinent species

Among all of the known polymorphs of In_2O_3 , the body-centered cubic bixbyite crystal structure consisting of eighty atoms in one unit cell represents the most thermodynamically stable phase. Our calculated bulk parameters were found to be in agreement with those of the model used by Walsh et al. [23]. The (110) surface was generated from this stable crystal bulk as our slab model (See Ref. [22] for details).

Prior to exploring the reaction steps, it is necessary to develop a deeper understanding of the processes involved in the adsorption of the relevant species onto the In_2O_3 surface. Figure 1 defines all the sites investigated on the In_2O_3 surface. The adsorption energies and geometries of all of the relevant species are listed in Table 1 and Fig. 2. In general, the O and C atoms of these species favor interactions with the lattice In and O atoms, respectively.

3.1.1. A1: CH_2O^*

As an important intermediate of MSR that is regularly observed in MSR experiments, this molecule was found to bind to the surface with its O and C atoms binding to the surface In_1 and O_1 atoms, respectively. The C–O bond length in this particular case was determined to be about 0.18 Å longer than the value observed in the isolated state of formaldehyde (1.21 Å). The C– O_1 and O– In_1 distances were found to be 1.46 and 2.08 Å,

Fig. 1. Site map (top and side views) of the $\text{In}_2\text{O}_3(110)$ surface. The bottom two layers have been neglected and the atoms of first layer have been represented by larger balls in the top view.

Table 1

Preferred adsorption sites, geometric parameters, and binding energies for the relevant species on $\text{In}_2\text{O}_3(110)$.

Species	Adsorption configuration	Bond details		Adsorption energy (eV)
		Bond	Length (Å)	
CH_2O^*	$\text{In}_1\text{-O}_1$ site through O and C	C–O	1.39	–1.65
		C– O_1	1.46	
		O– In_1	2.08	
		C– H_1	1.11	
		C– H_2	1.11	
CHO^*	$\text{In}_1\text{-O}_1$ site through O and C	C–O	1.27	–3.91
		C– O_1	1.28	
		O– In_1	2.22	
		C–H	1.10	
		C–O	1.25	
CO^* in $\text{COO}_{\text{lattice}}^*$	$\text{In}_1\text{-O}_1$ site through O and C	C– O_1	1.31	–0.85
		O– In_1	2.30	
		C–O	1.21	
CO^* in $\text{COO}_{\text{lattice}}^*$ (isomer)	$\text{In}_1\text{-O}_1$ site through C	C– O_1	1.28	–1.36
		C–O	1.28	
		O– In_1	2.35

Fig. 2. Side and top views of the most stable adsorption configurations of the relevant species on $\text{In}_2\text{O}_3(110)$.

respectively. In contrast to the weak adsorption reported on the pure Pd (–0.64 eV) [11] and PdIn surfaces (–0.13 eV) [21] the adsorption energy of CH_2O^* was calculated to be –1.65 eV, indicating that it would be difficult for this species to be desorbed during the reactions.

3.1.2. A2: CHO^*

Formyl is a radical-like species that prefers to be adsorbed onto the $\text{In}_1\text{-O}_1$ bridge site with its C and O atoms forming bonds with the O_1 and In_1 atoms, respectively. After being adsorbed, the $\text{In}_1\text{-O}_1$ bond length was found to have increased from a value of 2.35 to 2.62 Å. The angles of the O–C– O_1 and

C–O– In_1 bonds were calculated to be about 121.18° and 101.73°, respectively. In contrast to CH_2O^* , the C– O_1 bond length for CHO^* was much shorter (1.28 Å), whereas the O– In_1 distance was longer (2.22 Å). Among all of the relevant reaction intermediates [22], the adsorption energy of CHO^* was the third lowest with the value of –3.91 eV (larger than CH_2OH^* and H^*), which was in accordance with its radical nature. Interestingly, CHO^* possesses a much greater adsorption energy (–1.33 eV) on PdIn(110) [21], suggesting that the CHO^* produced during the MSR reaction on Pd/ In_2O_3 may prefer to locate at the oxide sites of the substrate.

3.1.3. A3: CO^* in $\text{COO}_{\text{lattice}}^*$

Once CHO^* gives out its H atom, CO^* species form above the $\text{In}_1\text{-O}_1$ bridge site. The C atom of the CO^* then connects to the lattice O atom (O_1), generating a new product namely $\text{COO}_{\text{lattice}}^*$. As shown in Fig. 2, this species behaves in a bidentate fashion because of its two O atoms, which can both bind with the surface In atoms. The CO portion lies almost parallel to the surface with a C–O bond length of 1.25 Å. The C– O_1 and O– In_1 distances were calculated to be 1.31 and 2.30 Å, respectively. Furthermore, the O–C– O_1 (117.34°) and C–O– In_1 (98.79°) angles in this configuration had changed very little compared with those of the CHO^* species. The adsorption energy of CO^* was determined to be –0.85 eV.

3.1.4. A4: CO^* in $\text{COO}_{\text{lattice}}^*$ (isomer)

Based on our NEB calculation results, we discovered that an isomer of $\text{COO}_{\text{lattice}}^*$ existed along the reaction pathway of adsorbed CO_2^* escaping from the surface to form CO_2 gas. Although the adsorption pattern of this material was also bidentate, this isomer points its O atom away from the surface. In this configuration, the C–O and C– O_1 bond lengths were found to be 1.21 and 1.28 Å, respectively, and the O–C– O_1 and O–C– In_1 bond angles were calculated to be 134.25° and 118.41°, respectively. The binding energy for CO in this isomer was about –0.51 eV lower than that of A3.

3.2. Reactions

To study the mechanism for the methanol decomposition reaction on the $\text{In}_2\text{O}_3(110)$ surface, we calculated the activation energy barriers and exothermicities for all possible elemental steps. During all of the calculated reactions, $\text{In}_1\text{-O}_1$ was found to be a special active site. To the best of our knowledge, no theoretical studies of this reaction have been reported in the literature. The calculation results are listed in Table 2, and the configurations of the initial state, transition state and final state are displayed in Fig. 3.

3.2.1. R1: $\text{CH}_2\text{O}^* \rightarrow \text{CHO}^* + \text{H}^*$

We started the reaction from CH_2O^* , which is considered to be an important intermediate during the MSR reaction. In the initial state, the reactant CH_2O^* was located at its most stable $\text{In}_1\text{-O}_1$ bridge site with one H atom pointing towards a lattice O_2 atom. In the transition state, the length of the breaking C–H bond reached 1.32 Å, and the distance between the H atom and

Table 2

Calculated activation and reaction energies for the elementary reactions on $\text{In}_2\text{O}_3(110)$ studied in this work.

Step no.	Elementary reaction	Activation energy E_a (eV)	Exothermicity ΔE (eV)
R1	$\text{CH}_2\text{O}^* \rightarrow \text{CHO}^* + \text{H}^*$	0.73	-1.07
R2	$\text{CH}_2\text{O}^* + \text{OH}^* \rightarrow \text{CHO}^* + \text{H}_2\text{O}^*$	0.15	-2.67
R3	$\text{CHO}^* \rightarrow \text{CO}^* + \text{H}^*$	1.91	0.48
R4	$\text{CHO}^* + \text{OH}^* \rightarrow \text{CO}^* + \text{H}_2\text{O}^*$	0.58	0.43
R5	$\text{COO}_{\text{lattice}}^* \rightarrow \text{COO}_{\text{lattice}}^*$ (isomer)	0.20	-0.51
R6	$\text{COO}_{\text{lattice}}^*$ (isomer) $\rightarrow \text{COO}_{\text{lattice}}$ (gas)	0.23	0.17

O_2 atom was computed to be about 1.36 Å. At the same time, the three distances between the O_2 -In bonds increased to 2.48, 2.21, and 2.21 Å. The product CHO^* was generated after the O_2 atom received the hydrogen atom, with the material being subsequently located at the In_1 - O_1 bridge site with the C and O atoms interacting with O_1 and In_1 atoms, respectively. In addition, the H atom of the CHO^* species was found to point away from the surface. Another H^* product was found to connect to the O_2 atom to form hydroxyl species with a H- O_1 distance of 0.98 Å. As shown in Table 2, this step must overcome an energy barrier of 0.73 eV, and the reaction was found to be exothermic (-1.07 eV).

3.2.2. R2: $\text{CH}_2\text{O}^* + \text{OH}^* \rightarrow \text{CHO}^* + \text{H}_2\text{O}^*$

The presence of an OH^* species derived from water decomposition [22] appeared to have a dramatic effect in terms of lowering the energy barriers associated with the dehydrogenation reactions. With the assistance of the hydroxyl species, the dehydrogenation of CH_2O^* was found to be much more facile than R1 with the energy barrier determined to be as low as 0.15 eV. In addition, the exothermicity of this reaction was reduced significantly from -1.07 (R1) to -2.67 eV, indicating that this reaction is much more thermodynamically favored. In the initial state, CH_2O^* and OH^* were coadsorbed on two different surface rows. The distance (H-O) between the dissociated H atom of CH_2O^* and the O atom of the hydroxyl OH^* was about 3.48 Å in the reactant, which was subsequently reduced to 1.88 Å in the transition state. In addition, the breaking C-H bond length was calculated to be 1.17 Å. Following the dissociation, the water produced was located on the top of In_3 atom with an O- In_3 distance of 2.38 Å and its hydrogen atom pointing towards the nearby lattice O_2 atom. In a similar manner to the R2 reaction, the CHO^* product was adsorbed at the In_1 - O_1 bridge site.

3.2.3. R3: $\text{CHO}^* \rightarrow \text{CO}^* + \text{H}^*$

The CHO^* species can be further dehydrogenated to CO^* . As shown in Fig. 3, the reactant CHO^* is positioned at the In_1 - O_1 bridge site, with C-O, C- O_1 , and O- In_1 distances of 1.27, 1.28, and 2.22 Å, respectively. During the transition state, the C-H bond length increased from its initial value of 1.10 to 1.47 Å, and the H- O_3 distance was found to be 1.32 Å. In addition, the O atom of the CHO^* species effectively broke loose of the restrictions of the lattice In_1 atom, as shown in Fig. 2. The O-C-H, O_1 -C-O, O_1 -C-H, and C-H- O_3 bond angles were found to be

Fig. 3. The atomic structures with side and top views of the initial state (IS), transition state (TS), and final state (FS) for each reaction on $\text{In}_2\text{O}_3(110)$ listed in Table 2.

125.09°, 123.83°, 111.03°, and 160.01°, respectively. In the final product, the O atom of the CO^* species was recombined with the lattice In_1 atom, whereas the C atom coordinated to the O_1 atom. The In-O, O-C, and C- O_1 distances were 2.30, 1.25, and

1.35 Å, respectively. In addition, the hydrogen atom produced was located on top of the O₃ atom. Compared with the R1 and R2 reactions, the energy barrier for this step was much higher (1.91 eV), and the reaction became endothermic with a reaction heat of 0.48 eV. It is noteworthy that the interaction of CO with the lattice O₁ appeared to form a bended CO₂ molecule (COO_{lattice}*), and this will be discussed in greater detail in reactions R5 and R6.

3.2.4. R4: $\text{CHO}^* + \text{OH}^* \rightarrow \text{CO}^* + \text{H}_2\text{O}^*$

In contrast to reaction R3, the participation of OH* significantly reduced the activation energy for the dehydrogenation of CHO*, and the barrier for this step was found to be only 0.58 eV, which is comparable to that of R1. The endothermicity of this reaction was equal to 0.43 eV. As shown in Fig. 4, this reaction was determined to be the rate-determining step. The co-adsorption of CHO* and OH* leads to the initial state. The surface OH* sits on top of the In₂ atom with a distance (O–H) of 2.44 Å between its O and the H atom of CHO*. This distance then changes to become 1.02 Å in the transition state. The C–H bond length was calculated to be 1.79 Å. Following the decomposition, the CO* and H₂O* species were located at the In₁–O₁ bridge site and on top of the In₂ atom, respectively. Recalling that the barrier for the formation of OH* from the decomposition of H₂O* is almost 0 eV, as calculated in our previous work [22], this is enough for the OH* to participate in the elementary steps of the R2 and R4 reactions.

3.2.5. R5: $\text{COO}_{\text{lattice}}^* \rightarrow \text{COO}_{\text{lattice}}^*(\text{isomer})$

Before desorption from the surface, the COO_{lattice}* species must undergo a process of conversion to a different isomer denoted as COO_{lattice}* (isomer). As shown in Table 2, this transformation only requires a low barrier of 0.20 eV with a reaction energy of –0.51 eV. As displayed in Fig. 3, during the transition state, the O–In₁ bond distance was 2.28 Å, and the O–C–O₁ bond angle was computed to be 140.51°. In the final state, the C atom is connected to the In₁ atom, and the O atom of the CO* points away from the surface.

3.2.6. R6: $\text{COO}_{\text{lattice}}^*(\text{isomer}) \rightarrow \text{COO}_{\text{lattice}}(\text{gas})$

Once the isomer of the COO_{lattice}* species is formed on the surface, it begins to desorb. In this step, the main change involves the scission of the C–In₁ and O₁–In₂ bonds. In the transition state, the lengths of these two bonds were found to be 2.99 and 2.35 Å, respectively. The O–C–O₁ angle then undergoes a change from initial value of 134.25° to 160.78°. In the final state, a linear CO₂ gas molecule was weakly adsorbed on the surface. This molecule can be readily cleaned out from the surface. Reaction R6 also possesses a low energy barrier with a value of 0.23 eV, and the ΔE was calculated to be 0.17 eV. The combination of reactions R5 and R6 provides a total energy barrier and exothermicity for CO₂ generation of 0.20 and –0.34 eV, respectively. Following the reaction, one of the O vacancies is yielded. The OH* species might then transfer to this site to assist in the recovery of the catalyst, although we did not study this process and will be exploring this possibility in greater detail in the future.

Fig. 4. Potential energy profile for the reaction from CH₂O to CO₂ on In₂O₃(110).

Based on the current calculation results, pure In₂O₃ appears to catalyze the MSR process to produce CO₂, therefore confirming the experimentally observed selectivity [16]. Although the bimetallic PdIn alloy is often believed to be beneficial for switching from CO-selective methanol dehydrogenation to CO₂-selective MSR, there are no confirmed reports in the literature pertaining to the mechanism of this suggested selectivity [21]. To develop a thorough understanding of the whole story of MSR in the context of this system, it is clear that further efforts will be needed to establish the mechanism of the MSR reaction on the PdIn alloy. The well-known synergistic effect between the alloy and the oxide may also influence the reaction. Given that the study of these effects is more involved, work towards developing a greater understanding in this area will have to be reserved for some future work. We believe that insights gained in the current study from studying the reaction networks on this surface will provide a solid platform for the design of new catalysts for the MSR process.

4. Conclusions

We have reported a periodic DFT study of the decomposition of formaldehyde to CO₂ on an In₂O₃(110) surface. The reaction between the adsorbed formaldehyde and the available hydroxyl generated from water splitting to produce CHO is much more facile than the direct dehydrogenation of formaldehyd. The CHO was consequently deprived a H atom by neighboring hydroxyls. Finally, the CO produced by the process seizes a lattice O atom to generate CO₂, which was readily desorbed from the surface. Our calculation results are consistent with the experimental observations, and will help to provide a better understand the catalytic role of In₂O₃ in terms of selectivity during the MSR process.

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Graphical Abstract

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Our calculation results indicate that In_2O_3 plays an important role in terms of the selectivity during methanol steam reforming (MSR), confirming the experimentally observed selectivity towards CO_2 .

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利用第一性原理研究氧化铟在甲醇水蒸气重整反应中的催化作用

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摘要: 基于第一性原理方法, 证明了甲醛在 $\text{In}_2\text{O}_3(110)$ 表面可以选择性地转化为 CO_2 。水分解得到的OH物种有利于甲醛脱氢得到CHO, 后者不易直接脱氢, 其H原子被周围的OH捕获生成CO和 H_2O 。最后, 相比较其从表面直接脱附, CO更容易获得一个晶格氧生成 CO_2 。计算结果表明, 在没有PdIn合金参与催化的甲醇水蒸气重整反应过程中, In_2O_3 确实扮演着非常重要的角色, 进而从理论上证实了甲醇在氧化铟表面选择性生成 CO_2 的实验结果。

关键词: 密度泛函理论; 甲醇水蒸气重整; 反应机理; 氧化铟

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