Applied Surface Science 386 (2016) 196–201

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Interface effects for the hydrogenation of CO_2 on $Pt_4/\gamma\text{-}Al_2O_3$

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ARTICLE INFO

Article history:
Received 12 January 2016
Received in revised form 28 April 2016
Accepted 5 June 2016
Available online 6 June 2016

Keywords:
CO_2 hydrogenation
$Pt_4/\gamma\text{-}Al_2O_3$
Pt(111)
Active site
Interface effects

ABSTRACT

Density Functional Theory was applied to investigate the hydrogenation of CO_2 to HCOO or CO on $Pt_4/\gamma\text{-}Al_2O_3(110)$ catalyst. It was found that the formation of CO is preferred to that of HCOO, kinetically and thermodynamically, indicating that methane can be formed on the Pt-based catalysts preferably. Furthermore, rather low an activation barrier (0.34 eV) for the formation of *trans*-COOH species was found, compared with that on Pt(111) surface (0.59 eV), showing that the interface between Pt_4 cluster and $\gamma\text{-}Al_2O_3(110)$ slab promotes the hydrogenation of CO_2. However, the activation barrier for the dissociation of *cis*-COOH species on the supported catalyst is 0.91 eV, which is much higher than that on pure metal surface (0.56 eV). An electronic transfer channel was found to reconcile the divergence. Our results indicate that $Pt/\gamma\text{-}Al_2O_3$ should be a promising candidate for the catalytic hydrogenation of CO_2 by adjusting the metal/support interface to balance the activation barriers for the formation of *trans*-COOH and the dissociation of *cis*-COOH species.

1. Introduction

Anthropogenic emission of CO_2 has brought about irreversible climate change, which is considered as a major threat to mankind [1]. However, increasing attention is paid on it since CO_2 is a promising substitute of toxic CO in C1-chemistry [2]. The recycling of emitted CO_2 to useful chemicals or liquid fuel can help to remit the greenhouse effects [3–5].

Selective hydrogenation of CO_2 to methanol or methane has been widely studied, among which HCOO (formate) and CO are two crucial intermediates. For instance, $Cu/ZnO/Al_2O_3$ was used by Rozovakii et al. [6] to catalyze the formation of methanol from syngas and formate was identified as the key intermediate. Collins et al. [7] also proposed that formate was the key intermediate for CO_2 hydrogenation to methanol on $Pd/\beta\text{-}Ga_2O_3$. In addition, CO is not only a product of reverse Water-Gas Shift (WGS) reaction, but also regarded as the key intermediate for methane formation [8–10]. Gupta et al. [11] found that CO was adsorbed on Ru^0 sites as a product of either CO_2 dissociation or hydrogenation. The $Ru\text{-}(CO)_{ad}$ species was further hydrogenated by co-adsorbed or gaseous hydrogen to form methane. Pan et al. [8] and Zhang et al. [12] studied the effect of surface hydroxyls on selective hydrogenation of CO_2 on $Ni/\gamma\text{-}Al_2O_3$ and $Cu/\gamma\text{-}Al_2O_3$ catalysts, respectively, also indicating that HCOO and CO are crucial intermediates to methanol and methane. All these studies suggest that the products of the initial steps in CO_2 hydrogenation determine the final products.

Although a large number of oxides supported metal catalysts are found to be active for CO_2 hydrogenation, including $Pd/\beta\text{-}Ga_2O_3$ [7], Cu/SiO_2 [13] and $Ni/\gamma\text{-}Al_2O_3$ [14], the microscopic mechanism at atomistic level is still unclear, especially the role of the metal/support interface. In our previous work [15], we have investigated the adsorption and the growth of Pt_n (n = 1-4) cluster on $\gamma\text{-}Al_2O_3(110)$ surface. Subsequently, in the present work, the elementary steps leading to the formation of formate or CO in CO_2 hydrogenation on $Pt/\gamma\text{-}Al_2O_3$ were investigated using density functional theory (DFT) calculations. In comparison, the CO_2 hydrogenation on Pt(111) surface was also investigated. These results can be helpful in understanding the effects of the metal/support interface on the hydrogenation of CO_2 on $Pt/\gamma\text{-}Al_2O_3$.

2. Model and methods

The $\gamma\text{-}Al_2O_3$ model described by Digne [16] was used for the Al_2O_3 surface in our calculations. Under the real catalytic conditions, more than 70% of the $\gamma\text{-}Al_2O_3(110)$ surface is exposed. The

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http://dx.doi.org/10.1016/j.apsusc.2016.06.018

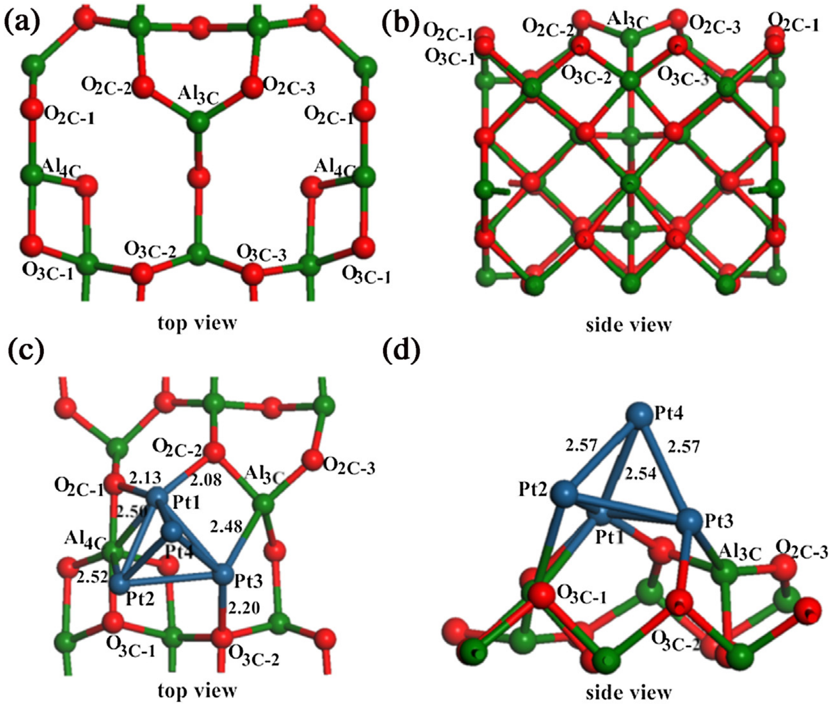

Fig. 1. The side and the top views of the γ-$Al_2O_3(110)$ surface and the Pt_4 cluster supported on the γ-$Al_2O_3(110)$ surface, S(Pt_4). Bond lengths are in Å. Green, red, and blue balls stand for Al, O, and Pt atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

non-spinel γ-Al_2O_3 $p(1 \times 1)$ model has been used to construct surfaces in our previous study of the adsorption of Pt_n (n = 1–4) on γ-$Al_2O_3(110)$ surface [15]. In the present study, a $p(2 \times 1)$supercell model with a dimension of 16.81 × 8.07 Å^2 was used. Twenty four Al_2O_3 unit cells were distributed in six atomic layers, with a 12 Å vacuum region separating the slabs in the perpendicular direction of the surface. In all calculations, the bottom two layers were frozen as their bulk positions, meanwhile the top four layers together with the Pt_4 cluster and adsorbed species were allowed to relax.

Fig. 1 shows the side and the top views of γ-$Al_2O_3(110)$ surface with topmost atoms labeled in the same way of our previous work [15]. On the virgin surface, 3-fold-coordinated aluminum (Al_{3c}), 4-fold-coordinated aluminum (Al_{4c}), 2-fold-coordinated oxygen (O_{2c}), and 3-fold coordinated oxygen (O_{3c}) atoms are exposed to the vacuum, and are unsaturated in coordination.

Periodic DFT calculations were performed with spin-polarized GGA + PBE [17] exchange-correlation functional implemented in the code VASP 5.3 [18,19]. The projected augmented wave method [20] was used to describe the core-electron interactions and the Kohn-Sham wave functions were expanded in the plane wave basis with a kinetic energy cutoff of 400 eV. Gaussian smearing method with a width 0.2 eV was used to determine the partial occupancies. The Brillouin zone was sampled with a 3 × 3 × 1 *k*-points mesh for the supercell, generated by the Monkhorst-Pack algorithm. The Hellmann-Feynman forces for all the relaxed atoms were converged to 0.03 eV/Å. Transition states in the elementary steps leading to the formation of formate or CO were determined in two steps: (1) the nudged elastic band method (NEB) [21] was used to search the possible reaction path way; (2) the climbing image NEB method was used to locate the saddle point. Imaginary frequency analysis was used to validate the transitional states.

The adsorption energy is defined as

$$\Delta E_{ads} = E\left(\mathrm{M/sub}\right) - [E(\mathrm{M}) + E(\mathrm{sub})]$$

where the E(M/sub), E(M) and E(sub) are the total energies of the substrate with adsorbed species, free adsorbate alone, and the substrate, respectively.

3. Results

3.1. Pt_4 supported on γ-$Al_2O_3(110)$ surface

Several sites on γ-$Al_2O_3(110)$ $p(2 \times 1)$ surface have been tested for the location of Pt_4 cluster. The most stable adsorbed configuration is shown in Fig. 1c–d. The adsorption energy is −4.67 eV, and the average Pt—Pt bond length is *ca.* 2.62 Å, both of which are quite consistent with the adsorption of Pt_4 cluster on $p(1 \times 1)$ surface [15]. We denotes the configuration as S(Pt_4), on which the hydrogenation of CO_2 will be investigated. In the S(Pt_4), three Pt atoms (Pt1, Pt2 and Pt3) in the bottom of the Pt_4 cluster interact with atoms of γ-$Al_2O_3(110)$ surface directly, forming two Pt1—O_{2C} bonds (2.13 and 2.08 Å), two Pt—O_{3C} bonds (2.29 and 2.20 Å), two Pt—Al_{4C} bonds (2.50 and 2.52 Å), and one Pt3—Al_{3C} bond (2.48 Å).

3.2. Hydrogenation of CO_2 on S(Pt_4)

It is believed that, for the hydrogenation of CO_2, the co-adsorption of CO_2 molecule and H atom is prerequisite. Different initial co-adsorption configurations of CO_2 and H on S(Pt_4) have been investigated (see the supporting information) and only the most stable one (denoted as S_1) will be reported. The S_1 configuration was regarded as the reference state for CO_2 hydrogenation to HCOO (formate) in Section 3.2.1 and to CO in Section 3.2.2. For clarity, the intermediates (IM), the transition states (TS) and the products involved in CO_2 hydrogenation on S(Pt_4) were prefixed with S. The co-adsorption energy of H atom and CO_2 molecule in S_1 is −1.52 eV.