



Isopropanol adsorption on γ -Al₂O₃ surfaces: A computational study

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ABSTRACT

The adsorption of isopropanol on the clean and hydrated γ -Al₂O₃ (1 0 0) and (1 1 0) surfaces was investigated at the level of density functional theory. It is found that isopropanol interacts with the γ -Al₂O₃ surface via its –OH group. The most stable adsorption site on the (1 0 0) and (1 1 0) surfaces is Al(3) and Al(4), respectively, with the –OH group of isopropanol orientated to surface oxygen atom. The computed adsorption energies correlate well with the energy level of the surface Lewis sites. On the (1 0 0) surface with OH coverage of 8.8, Al(5) is the most stable adsorption site. On the (1 1 0) surface with OH coverages of 8.9 and 11.8, Al(2) and Al(1) are the available sites for adsorption. It is to note that water has much larger adsorption energies than isopropanol on both surfaces.

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1. Introduction

γ -Alumina (Al₂O₃) is an important industrial material widely used as adsorbent, catalyst and especially as catalyst support [1,2]. The catalytic properties of alumina for ethanol dehydration had been discovered in 1797 [3]. Despite many investigations into the catalytic processes of dehydration and dehydrogenation of alcohols to olefins, ethers and ketones over γ -Al₂O₃, the mechanisms of these reactions were not well established yet [4–14].

On the basis of their excellent work on dehydration of alcohols over Al₂O₃ in the 1960s to 1970s, Knözinger et al. proposed the reaction mechanism models, but the deduced kinetic equations did not fit the experimental data for the reaction of ethanol over Al₂O₃ [7,8]. On the basis of the study of ¹⁸O-labeled alcohol adsorption on γ -Al₂O₃ with temperature-programmed desorption technology, DeCanio et al. found that the dissociative adsorption of alcohol on Lewis acid sites and the nucleophilic attack by a surface oxide on an alcohol are the paths for alkoxide formation [10].

Due to its practical importance, this field also attracted considerable theoretical interests [4,15–17]. De Vito et al. computed methanol adsorption on the (1 1 0) surface with a [Al₃O₉H₁₀]⁺ γ -Al₂O₃ cluster and concluded that methanol adsorbs on a tetrahedral aluminum ion forming a covalent bond [17]. However, the latest study revealed that the tiny [Al₃O₉H₁₀]⁺ cluster is not large enough to describe the different coordinated surface Al atoms of γ -Al₂O₃ [18,19]. Cai and Sohlberg studied the adsorption of alcohols on the energetically preferred γ -Al₂O₃ (1 1 0 C) using semi-empirical PM3 method and a defective spinel-like Al₄₈O₇₂ cluster model [4], and proposed that the formation of alkoxide by abstracting the alcohol –OH proton is favored over alkoxide production through C–OH bond scission. However, they used fixed γ -Al₂O₃ cluster in their calculation and neglected the effects of surface reconstruction. They also did not consider the role of surface hydroxyl groups. Clayborne et al. studied the possible interactions between methanol and the double oxygen bridged Al₂O₂(OH)₂ group, and concluded that the reaction should occur on the coupled surface acid-base sites [15].

It is noteworthy that all these calculations are based on limited cluster models, which are either too small or fixed in bulk structures, and no periodic slab models were used to describe the properties of γ -Al₂O₃ surfaces. In addition, previous theoretical calculations mainly pay attention to methanol adsorption for dehydration and decomposition. As the simplest secondary alcohol, isopropanol has the advantage over methanol for the study of alcohol dehydration to olefins and ethers, and especially dehy-

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drogenation to ketones. Isopropanol is widely used for transfer hydrogenation [12,13,20,21]. Under real reaction conditions of alcohol dehydrogenation, dehydration and decomposition (350–780 K), and pretreated conditions of γ - Al_2O_3 (350–830 K) [5–15,21], γ - Al_2O_3 surfaces have different coverage of surface hydroxyls [19]. Here, we present a detailed theoretical study on isopropanol adsorption on both clean and hydrated γ - Al_2O_3 (1 0 0) and (1 1 0) surfaces for a fundamental understanding into the dehydration and dehydrogenation reactions of alcohol over γ - Al_2O_3 .

2. Methods and models

2.1. Methods

All calculations were performed in the framework of density functional theory (DFT) as implemented in the Vienna Ab Initio Simulation Package (VASP) [22,23]. The PW91 generalized-corrected exchange and correlation functional was used [24]. Atomic cores are described with the projected augmented wave method (PAW) [25,26]. The wave functions are developed on a basis set of plane waves. Periodic boundary conditions are set. All these methods were tested and validated [19,27,28]. Brillouin zone integration is converged with $3 \times 3 \times 1$ and $5 \times 5 \times 1$ k -points mesh respectively for the (1 0 0) and (1 1 0) surfaces, generated by the Monkhorst–Pack algorithm. The cutoff energy is 400 eV, which ensures a better convergence of the total energy. Taking superposition of atomic charge densities, wave function arrays were filled with random numbers.

2.2. Models

Many types of transition Al_2O_3 have been reported in literature [1,19,29–37]. γ - Al_2O_3 is one of the most widely used catalyst and support in alcohol Al_2O_3 reaction system [1,12–15]. However, no general statement about the structure of γ - Al_2O_3 has been made. From the numerous literatures, we examined three typical γ - Al_2O_3 structures; (a) the traditional defective spinel structure, (b) the Paglia structure and (c) the Digne structure [1,19,31,32]. Although the defective spinel structure was usually used to describe the γ - Al_2O_3 structure [33], the latest theoretical and experimental studies do not favor it [19,34–37]. The Digne structure, proposed on the basis of DFT study of topotactic transformation of hydrated boehmite into γ - Al_2O_3 , agrees well with the experimental data, i.e., NMR, XRD, bulk modulus, electronic density and especially the acid-base surface properties characterized by OH-stretching vibrations [19,34]. Therefore, we take the Digne structure as our model, and two main orientations under real catalytic conditions, (1 0 0) and (1 1 0) [19,38], were considered. It has been further found that the most stable termination of the (1 0 0) surface of γ - Al_2O_3 contains 8.8 OH/nm^2 at around 500 K and is fully dehydrated at 600 K. The most stable termination of the (1 1 0) surface contains about 8.9 – 11.8 OH/nm^2 at around 500 K and is fully dehydrated at 1150 K [19]. Therefore, the hydrated surfaces are examined with OH coverage of 8.8 OH/nm^2 for the (1 0 0) surface and 8.9 – 11.8 OH/nm^2 for the (1 1 0) surface. Since the *gauche* conformation of isopropanol is more stable than the *anti* one in liquid and gas phase [39,40], the former is used. The calculated C–O and O–H bond lengths of free isopropanol are 1.459 and 0.991 Å, respectively.

All calculations were performed on four-layer periodic slab model, which has been tested and proved reliable for H_2 and CH_4 adsorption [28]. To minimize the interaction of adsorbates of the neighboring slabs, $p(2 \times 1)$ and $p(1 \times 1)$ slabs, which contain sixteen and eight Al_2O_3 units, are chosen for the (1 0 0) and (1 1 0) surfaces, respectively. Two surface layers of the slabs and the adsorbed

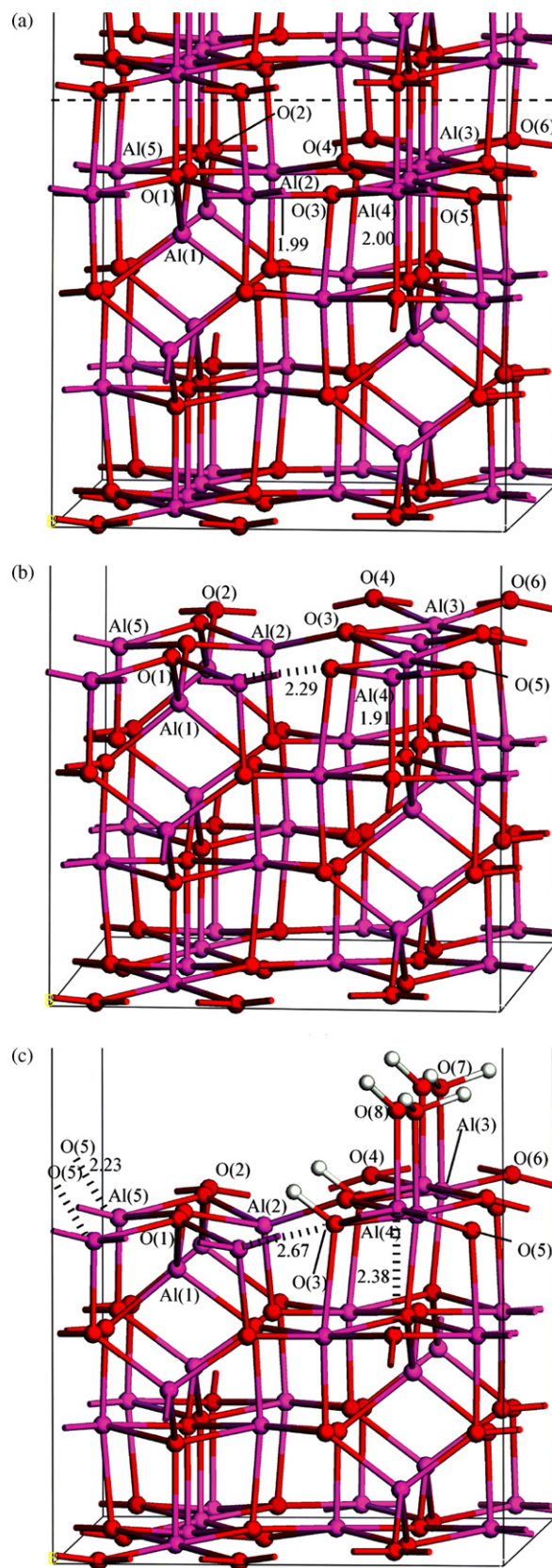


Fig. 1. Side views of $p(2 \times 1)$ cell for γ - Al_2O_3 (1 0 0): (a) un-relaxed (under dotted line), (b) relaxed, (c) hydrated with $\theta = 8.8 \text{ OH/nm}^2$ (oxygen in red and aluminum in violet). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

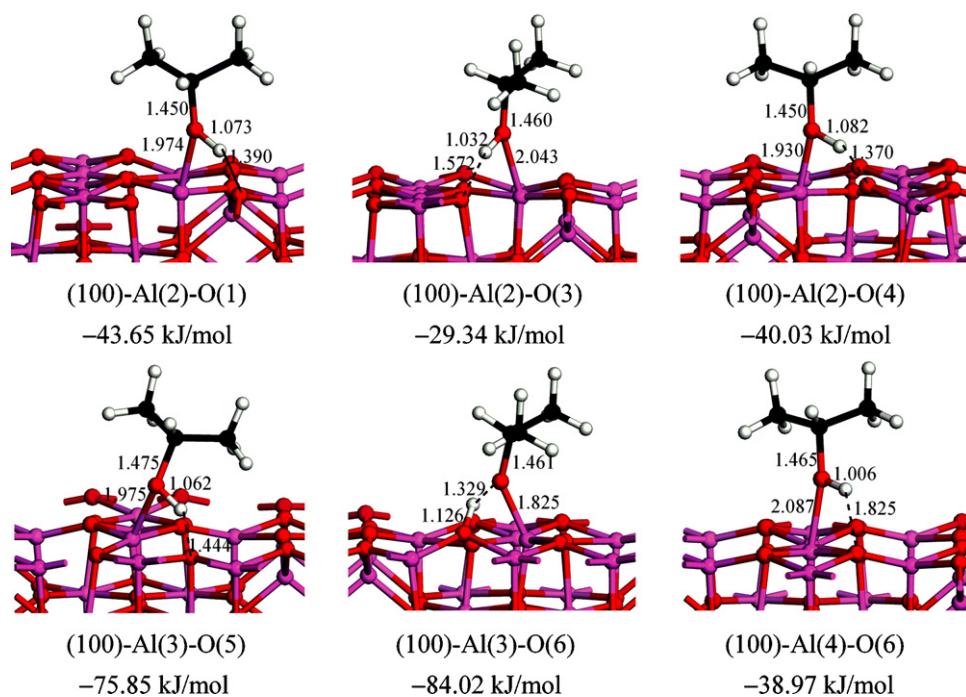


Fig. 2. Optimized adsorption configuration of isopropanol on the dehydrated γ - Al_2O_3 (100) surface (bond distances in angstrom) and the computed adsorption energies.

molecule were fully relaxed. The vacuum zone between the slabs was set to 15 Å. Dipole corrections have little differences in geometries and the resulted energetic corrections are about 2 kJ/mol. Thus, dipole corrections have not been applied.

The adsorption energy of isopropanol on the surface is given by $\Delta E = E(\text{isopropanol}/\gamma\text{-Al}_2\text{O}_3) - [E(\text{isopropanol}) + E(\gamma\text{-Al}_2\text{O}_3)]$, where $E(\text{isopropanol}/\gamma\text{-Al}_2\text{O}_3)$, $E(\text{isopropanol})$ and $E(\gamma\text{-Al}_2\text{O}_3)$ are the total energies for the slab with adsorbed isopropanol on the surface, free isopropanol molecule, and slab of the $\gamma\text{-Al}_2\text{O}_3$ surface, respectively.

3. Results

3.1. Clean $\gamma\text{-Al}_2\text{O}_3$ (100) surface

Fig. 1 shows the side views of $p(2 \times 1)$ $\gamma\text{-Al}_2\text{O}_3$ (100) slab. The un-relaxed (under the dotted line) and relaxed surfaces are displayed in Fig. 1a and b, respectively. Detailed comparison reveals the relaxation and reconstruction of the surface. In bulk, there are two Al centers, one is tetra-coordinated and one is hexa-coordinated. On the un-relaxed (100) surface, Al(1) is tetra-coordinated and in a position below the surface plane; and therefore not available for adsorption, while Al(2)–Al(5) are exposed on the surface and become penta-coordinated (Al_V). On the relaxed surface, the Al(2)–O(3) and Al(5)–O(5) distances are elongated to 2.29 Å, much longer than the un-relaxed distances of 1.99 Å, Al(2) and Al(5) become distorted penta-coordinated (Al_V). On the contrary, Al(3) and Al(4) are kept penta-coordinated (Al_V). Obviously, O(3) and O(5) are in distorted four-coordinated environments and other oxygen atoms are tri-coordinated. It is to note that Al(2) and Al(5) are equal on the dehydrated (100) surface, while Al(3) and Al(4) are different in chemical environments. We considered only the possible configurations of isopropanol adsorbed on Al(2), Al(3) and Al(4).

Fig. 2 shows six chemisorption configurations with oxygen atom of hydroxyl group coordinated to surface Al atom and hydrogen

atom of hydroxyl orientated to surface oxygen atom. Al(3) is the most stable site for isopropanol adsorption with the adsorption energy in the range of -75.85 to -84.02 kJ/mol, while those at Al(2) and Al(4) are much less stable. It is to note that (100)-Al(3)-O(6) is a dissociative adsorption model, in which the H_{ad} atom of the O–H group is extracted by O(6) atom. The O(6)– H_{ad} distance is 1.126 Å and the $\text{H}_{\text{ad}}\text{--O}_{\text{ad}}$ distance is elongated to 1.329 Å.

Attempts to get adsorption configurations of isopropanol only via either its hydroxyl H atom interacting with the surface Brønsted base site or its methyl groups failed. Free optimization resulted in configuration in simultaneous interaction of its hydroxyl O and H atoms with both surface aluminum and oxygen sites, respectively.

3.2. Clean $\gamma\text{-Al}_2\text{O}_3$ (110) surface

Fig. 3 shows the side views of $p(1 \times 1)$ $\gamma\text{-Al}_2\text{O}_3$ (110) slab. The un-relaxed (under the dotted line) and relaxed surfaces are displayed in Fig. 3a and b, respectively. In $\gamma\text{-Al}_2\text{O}_3$ bulk (Fig. 3a), Al(1–3) atoms are in octahedral centers and Al(4) is in tetrahedral center. On the un-relaxed surface, it is obvious that Al(1–3) atoms are tetra-coordinated (Al_{IV}) and Al(4) is tri-coordinated (Al_{III}). After relaxation (Fig. 3b), all the surface oxygen atoms move outward, especially O(4–6). Al(4) forms a planar AlO_3 surface species [19]. Since the chemical environments of Al(1) and Al(2) are equal, we considered only the possible configurations of isopropanol adsorbed on Al(1), Al(3) and Al(4).

The optimized chemisorption configurations are shown in Fig. 4. The strongest adsorption site is Al(4) with the largest adsorption energy of -190.56 kJ/mol, while Al(1) and Al(3) have much lower adsorption energies. It is to note that (110)-Al(4)-O(3) has molecular adsorbed isopropanol, and the $\text{O}_{\text{ad}}\text{--H}_{\text{ad}}$ and O(3)– H_{ad} distances are 1.053 and 1.577 Å, respectively.

Another interesting result on this surface is the bridged adsorption between Al(1) and Al(2). Bridge-alkoxide has been detected in experiments [9,21,41], but not reported in the previous calculations

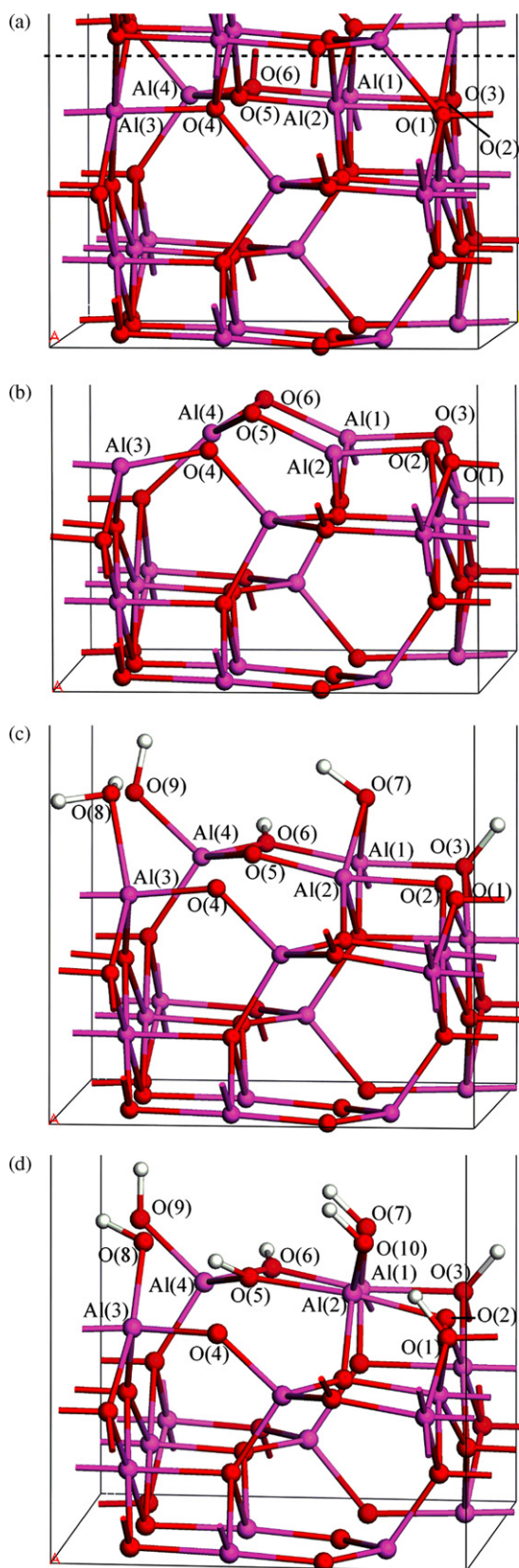


Fig. 3. Side views of $p(1 \times 1)$ cell for $\gamma\text{-Al}_2\text{O}_3$ (110): (a) un-relaxed (under dotted line), (b) relaxed, (c) hydrated with $\theta = 8.9 \text{ OH/nm}^2$, (d) hydrated with $\theta = 11.8 \text{ OH/nm}^2$ (oxygen in red and aluminum in violet). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

[4,15,17]. In (110)-Al(1,2)-O(5), due to the weak interaction of the new formed $\text{O}_{\text{ad}}\text{-Al}(1)$ and $\text{O}_{\text{ad}}\text{-Al}(2)$ bonds to the $\text{O}_{\text{ad}}\text{-H}_{\text{ad}}$ bond and strong basicity of O(5), the H atom is extracted from the isopropanol –OH group. Nevertheless, this bridged form is much less stable than (110)-Al(4)-O(3) by 77.71 kJ/mol.

Digne et al has reported the energy level of the surface Lewis acid site for both the (100) and (110) surfaces [19]. As given in Table 1, the adsorption energy correlates well with the energy level of the acid site, i.e., the stronger the Lewis acidity of the Al site, the stronger the adsorption on it.

3.3. Hydrated $\gamma\text{-Al}_2\text{O}_3$ (100) and (110) surfaces

In real reaction systems, water is always available, and it is therefore necessary to consider the influence of surface water on the properties of catalysts and catalytic reaction. For that we have used the hydrated (100) $\gamma\text{-Al}_2\text{O}_3$ surface with OH coverage of 8.8 OH/nm^2 reported by Digne et al (Fig. 1c) [19]. Compared to the relaxed clean (100) surface, Al(3) has an adsorbed water ($\text{O}(7)\text{H}_2$), while Al(4) has an adsorbed $\text{O}(8)\text{H}$ and one hydrogen atom is at surface O(3) forming in-surface $\text{O}(3)\text{H}$, and Al(4) moves outward. In this case, the chemical environment of Al(2) and Al(5) becomes different due to the influence of surface hydroxyls. Since Al(3) and Al(4) are covered, only Al(2) and Al(5) are available for further adsorption. The optimized chemisorption configurations are shown in Fig. 5.

On the hydrated (100) surface, the adsorption energy at (100) ($\theta = 8.8$)-Al(2)-O(1) is -40.29 kJ/mol , very close to that (-43.65 kJ/mol) of the clean surface (100)-Al(2)-O(1). The difference is that the former has dissociative adsorption and the latter has molecular adsorption. On Al(5), the most stable adsorption configuration is (100) ($\theta = 8.8$)-Al(5)-O(8) with adsorption energy of -70.50 kJ/mol , and this large adsorption energy is due to the much strong hydrogen bonding interaction between the proton of isopropanol–OH group and the surface hydroxyl O atom (1.512 \AA). On the contrary, (100) ($\theta = 8.8$)-Al(5)-O(1) and (100) ($\theta = 8.8$)-Al(5)-O(5) have hydrogen bonding interaction between isopropanol–OH group and surface oxygen atoms and the adsorption energies are -18.90 and -16.90 kJ/mol , respectively.

The hydrated (110) $\gamma\text{-Al}_2\text{O}_3$ surfaces with OH coverage of 8.9 and 11.8 OH/nm^2 , reported by Digne et al. [19], are shown in Fig. 3c and d, respectively. Compared to the relaxed clean (110) surface, water adsorption results in serious surface reconstruction. In Fig. 3c, three water molecules are necessary for OH coverage of 8.9 OH/nm^2 on the (110) surface. After water adsorption, Al(3) has an adsorbed $\text{O}(8)\text{H}_2$, while Al(4) has an adsorbed $\text{O}(9)\text{H}$. On the contrary, Al(1) and Al(2) share one bridge-like $\text{O}(7)\text{H}$ group. Two dissociated hydrogen atoms move to surface O(3) and O(6) and form in-surface $\text{O}(3)\text{H}$ and $\text{O}(6)\text{H}$, respectively. It is to note the $\text{O}(9)\text{H}$ group makes Al(4) move to a tetrahedral position, while is not available for adsorption. The $\text{O}(8)\text{H}_2$ group on Al(3) also prevents adsorption. The results show that both Al(1) and Al(2) have adsorption activity for isopropanol. As O(3) atom attaches with a surface H, only molecular adsorption is formed on Al(1).

Table 1

Energy levels of the surface Al Lewis sites and the corresponding adsorption energies.

Site	E (eV) ^a	ΔE_{ads} (kJ/mol)
(100)-Al(2)	-0.7	-43.65
(100)-Al(3)	-1.6	-84.02
(100)-Al(4)	+0.1	-38.97
(110)-Al(1)	-1.1	-96.16
(110)-Al(3)	-1.5	-138.71
(110)-Al(4)	-2.5	-190.56

^a Ref. [19].

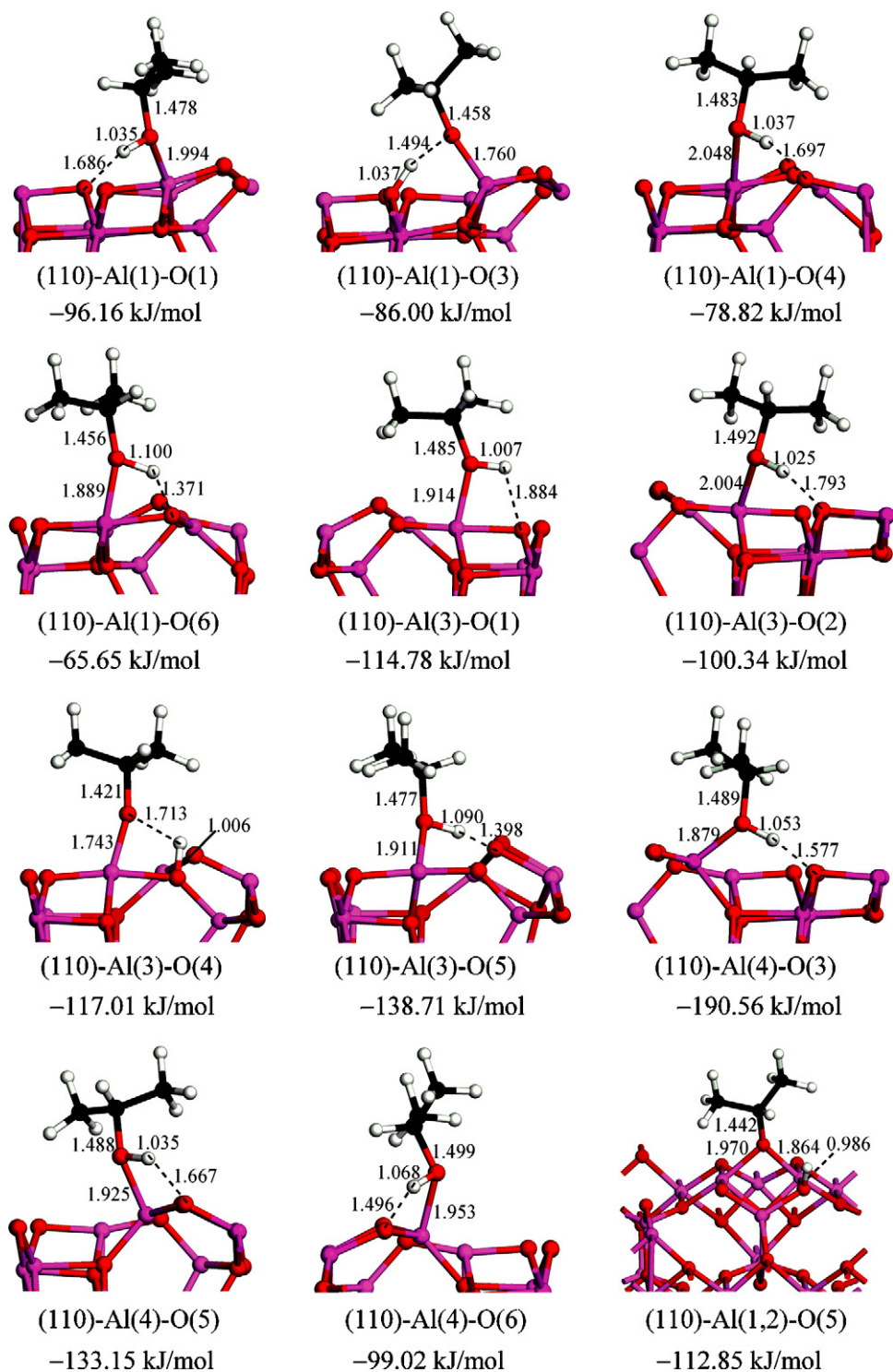


Fig. 4. Optimized adsorption configuration of isopropanol on the dehydrated γ -Al₂O₃ (110) surface (bond distances in angstrom) and the computed adsorption energies.

The adsorption energy of (110) ($\theta=8.9$)-Al(1)-O(7) is -53.08 kJ/mol, about 30 kJ/mol lower than on the clean surface. In (110) ($\theta=8.9$)-Al(2)-O(2) the H_{ad} of -OH group is extracted by the O(2) atom and has an adsorption energy of -119.27 kJ/mol. It indicates that the adsorption activity of the clean surface oxygen atom is not seriously influenced by surface hydroxyls.

On the hydrated (110) surface with 11.8 OH/nm², one more water molecule is adsorbed at Al(2) with the formation of O(10)H and O(1)H. On this surface, all surface O atoms are covered with H

atoms, this hydrated surface loss the ability of dehydrogenation to form dissociative adsorption. The only available site for adsorption is Al(1), and the adsorption energy of (110) ($\theta=11.8$)-Al(1)-O(10) is -84.83 kJ/mol.

3.4. Competitive adsorption of alcohol and water

The strongest adsorption energies for isopropanol on the clean γ -Al₂O₃ (100) and (110) surfaces are -84 and -190 kJ/mol, respectively, and those of water are -105 and -240 kJ/mol, respec-

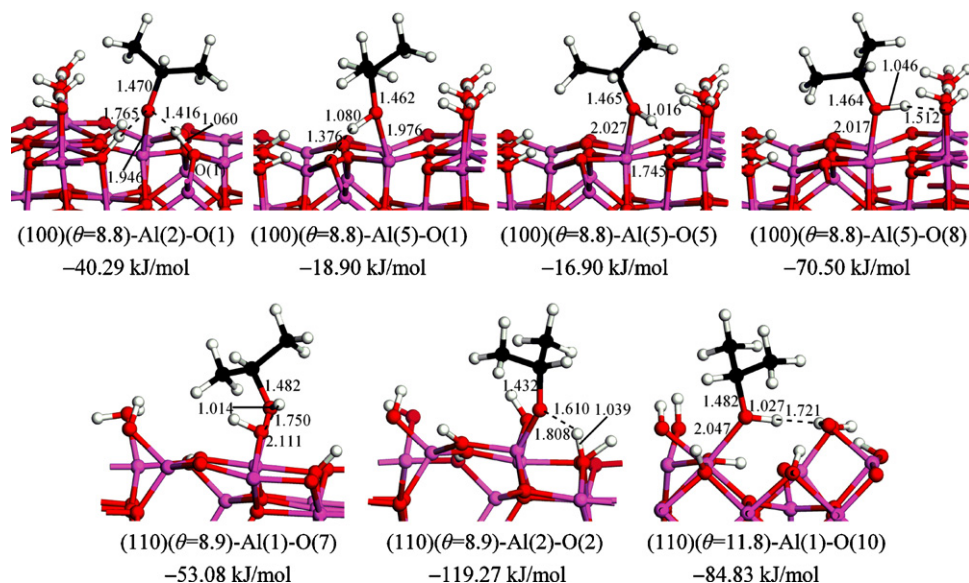


Fig. 5. Optimized adsorption configuration of isopropanol on the hydrated γ - Al_2O_3 (100) and (110) surface (bond distances in angstrom) and the computed adsorption energies.

tively [19]. It implies that water in reaction is more competitive than isopropanol adsorption. This explains reasonably the experimental results by Clayborne et al. [15]. They used 95% ethanol and 100% other alcohols to make the TPD samples, and found that the adsorption amount of ethanol is about 10% lower than that of other alcohols.

4. Conclusion

The adsorption of isopropanol on the clean and hydrated (100) and (110) surfaces of γ - Al_2O_3 has been investigated by means of density functional theory calculations. In our calculation, all possible adsorption configurations have been considered. It is found that isopropanol interacts with the γ - Al_2O_3 surface via its $-\text{OH}$ group.

On the clean (100) surface, the most stable adsorption site is Al(3) for both dissociatively adsorbed isopropanol and molecular adsorbed isopropanol in close energy and the difference is the orientation of the hydrogen to surface oxygen atom (O(5) vs. O(6)). On the clean (110) surface, the most stable adsorption site is Al(4) with molecular adsorbed isopropanol and OH orientated to surface O(3), while other adsorption sites have much lower adsorption and are therefore thermodynamically not competitive. The computed adsorption energies correlate well with the energy level of the surface Lewis sites.

On the hydrated (100) surface with OH coverage of 8.8, the most stable adsorption site is Al(5), with hydroxyl H atom of isopropanol interacting with the O atom of surface hydroxyl group. On the hydrated (110) surface with OH coverage of 8.9 and 11.8, the Al(2) and Al(1) are the available sites for adsorption, respectively. It is to note that water has larger adsorption energies than isopropanol on both surfaces.

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