

Adsorption of alcohols on γ -alumina (1 1 0 C)

Shuhui Cai ^{a,b}, Karl Sohlberg ^{b,*}

^a Department of Physics, Xiamen University, Xiamen 361005, PR China

^b Department of Chemistry, Drexel University, 3141 Chestnut Street, Philadelphia, PA 19104, USA

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Abstract

Adsorption of methanol, ethanol, propanol and isopropanol on the γ -alumina (1 1 0 C) surface is investigated with semi-empirical (PM3) cluster calculations. It is found that all four alcohols chemisorb to the alumina surface when they come close to the surface with suitable orientation. The chemisorption is an exothermic process when the OH hydrogen interacts with a surface oxygen atom that is in turn close to a cation vacancy. In this case only O–H interaction is required for successful dehydrogenation. If the surface oxygen has no adjacent vacancies, both the oxygen and hydrogen from the alcohol OH must interact with the surface for successful dehydrogenation. Alkoxide formation by abstraction of the alcohol OH proton is found to be favored over alkoxide production by nucleophilic attack of the alcohol C_α by a surface Lewis base site followed by C–OH bond scission.

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1. Introduction

The catalytic properties of alumina for alcohol dehydration have been exploited for more than 200 years [1–4]. Today, alcohol dehydration with alumina-based catalysts to form olefins and/or ethers for starting materials is an important industrial process [1,5]. Future applications of alcohol dehydration catalysts could include the conversion of biomass-derived alcohols into transportation fuels and other energy products. While the complexity of heterogeneous catalysts for alcohol dehydration continues to increase as the technology advances, dehydration on transitional aluminas remains a prototypical reaction of alcohol dehydration by heterogeneous

catalysis. An atomic-scale understanding of the reaction pathways would facilitate the design of improved catalysts.

Although different views are held concerning the mechanism of the heterogeneously catalyzed dehydration of alcohols on aluminum oxide, it is generally believed that the mechanism initiates with the direct interaction of the hydroxyl group of the alcohol with the oxide surface [6]. Acidic and/or basic surface sites are assumed to take part in the dehydration procedure. At least three possible hydrogen-bonding interactions are easily envisioned, active H-bonding, passive H-bonding, and a bridging structure involving both active and passive H-bonding [1]. Another chemically obvious interaction is through a four-center structure whereby the O atom of the alcohol OH interacts with a surface Lewis acid site (surface Al), and the OH proton interacts with a Lewis base site (surface oxygen). DeCanio et al. postulated that methanol is

* Corresponding author. Tel.: +1-215-895-2653;

fax: +1-215-895-1265.

E-mail address: sohlbergk@drexel.edu (K. Sohlberg).

dissociatively adsorbed on surface acid–base pairs leading to the formation of CH_3^+ and OH^- species in parallel with the production of CH_3O^- and H^+ species [6]. Temperature-programmed desorption (TPD) results suggest that there are two routes to alkoxide (CH_3O^- and $\text{C}_2\text{H}_5\text{O}^-$) formation: one involving a direct reaction of the alcohol at a Lewis acid site and the other involving reaction of the alcohol with a nucleophilic surface base site [6]. Knözinger and DeCanio et al. showed that adjacent acid–base sites are required for ether formation, but only strong acid sites are required for olefin formation [1,6]. They also showed that ether formation occurs via a bimolecular reaction between an alkoxide species and a strongly adsorbed alcohol. A complete description of the mechanism of dehydration, in particular the roles of the surface acid and base sites, has not been definitively established.

Most previous theoretical investigations of adsorption on γ -alumina focused on the Lewis acidity of surface Al sites [7–9] and their reactivity with water [10–12], hydrogen sulfide [10], carbon monoxide [10], ammonia [11], pyridine [11], etc. In a previous calculation of the adsorption of methanol [13], a simple cluster $[\text{Al}_3\text{O}_9\text{H}_{10}]^+$ was used to model the alumina surface. In addition, deprotonation of methanol was assumed to occur first and methoxyl-ion was directly positioned in the vicinity of tetrahedrally coordinated Al. Al atoms at tetrahedral sites have subsequently been shown to be absent from the γ -alumina surface [14,15].

Herein we report the results of calculations designed to investigate the preferred adsorption sites for alcohols on γ -alumina (1 1 0 C) surfaces using an $\text{Al}_{48}\text{O}_{72}$ cluster model of γ -alumina that includes all atoms up to and including second-nearest neighbors of the adsorption site. We found that all four alcohols studied chemisorb to the alumina surface when they come close to surface with suitable orientation. Only hydrogen of the alcohol OH group is required to interact with surface oxygen for successful dehydrogenation when the surface oxygen is close to a cation vacancy. If there are no vacancies near the surface oxygen, both the alcohol oxygen and hydrogen must interact with the surface. We also investigate the two possible routes to alkoxide formation proposed in [6]. The direct reaction with a Lewis acid site is found to be a lower energy path to alkoxide

formation than nucleophilic attack by a surface Lewis base.

2. Computational method and models

γ -Alumina has been described as a defect spinel structure (space group $Fd\bar{3}m$) [16]. Aluminum cations are distributed over the octahedral (O_h) and tetrahedral (T_d) interstitial sites in the oxygen anion sublattice. The 8/3 cation vacancies per cubic unit cell (one in nine spinel cation sites) are required to maintain Al_2O_3 stoichiometry. Although early surface studies focused on the (1 0 0) face, it is now known that (1 1 0) face of γ -alumina is preferentially exposed [17–19]. However, there are two (1 1 0) layers in γ -alumina, denoted (1 1 0 C) and (1 1 0 D) [17]. Structural relaxations of these two surfaces show that it is energetically preferred to expose the (1 1 0 C) layer [14]. While simple cleavage of bulk γ -alumina will produce both three-coordinated Al (those at T_d sites) and four-coordinated Al (those at O_h sites) at the (1 1 0 C) surface, a spontaneous reconstruction depletes the three-coordinated Al from the surface [14,15], and only four-coordinated Al are observed [20]. The adsorption of CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_3\text{H}_7\text{OH}$ and $(\text{CH}_3)_2\text{CHOH}$ on the γ -alumina (1 1 0 C) surface was investigated with electronic structure calculations based on the semi-empirical PM3 Hamiltonian [21] and an $\text{Al}_{48}\text{O}_{72}$ cluster model of γ -alumina (see Fig. 1). Semi-empirical models have been used effectively in theoretical investigations of similar systems, including adsorption on metal oxide surfaces [8,22,23], and shown to lead to qualitative conclusions consistent with ab initio calculations (see, for example, [8,24–27]). We have further validated the reliability of the PM3 approximation for the present study by performing layered ab initio/semi-empirical calculations for key results. The much lower computational cost of semi-empirical calculations allows for modeling a cluster that includes all atoms up to and including second-nearest neighbors of the adsorption site, much larger than is currently practical with first-principles methods. To our knowledge, all cluster models used previously in modeling γ -alumina surfaces were smaller, including only a few aluminum atoms regardless of whether semi-empirical or ab initio methods were employed [8,9]. The cluster model

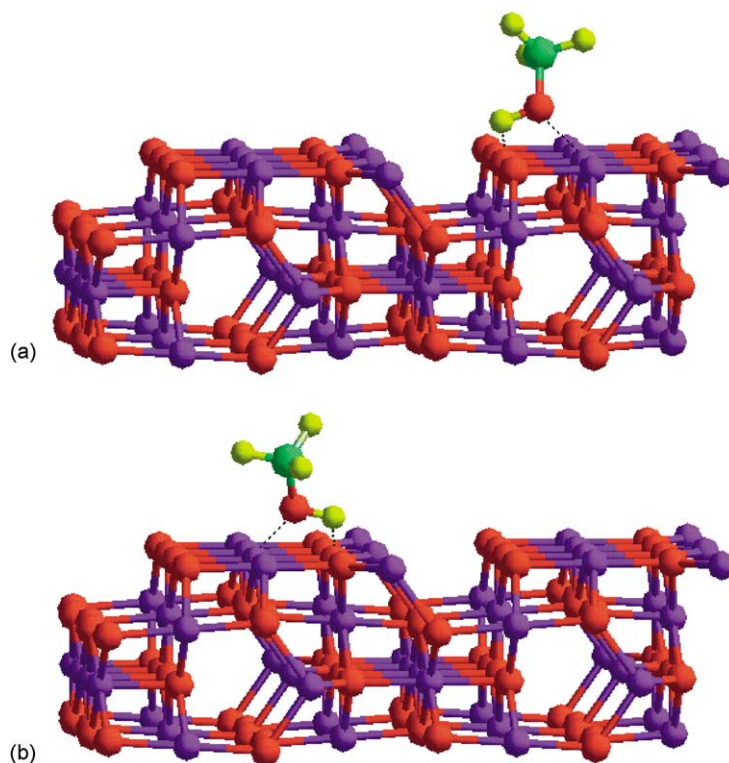


Fig. 1. Two types of initial adsorption configurations: (a) site A (surface O atom has adjacent vacancy); (b) site B (surface O atom has no adjacent vacancies). Dash lines indicate short atomic distances (close to normal bond lengths).

employed here is much larger than any used previously and ensures that the coordination environments of the surface atoms interacting with adsorbate, and their nearest neighbors, are representative of those on the surface of a periodic crystal.

The cluster was constructed based on a defect-free γ -alumina supercell $\text{Al}_{48}\text{O}_{64}$ ($\text{Al}_{16}\text{Al}_{32}\text{O}_{64}$ in the spinel notation) defined by

$$\mathbf{a} = -\mathbf{a}_\gamma + \mathbf{b}_\gamma$$

$$\mathbf{b} = -0.5\mathbf{a}_\gamma - 0.5\mathbf{b}_\gamma$$

$$\mathbf{c} = 2\mathbf{a}_\gamma$$

where \mathbf{a}_γ , \mathbf{b}_γ and \mathbf{c}_γ are the basis vectors of cubic γ -alumina. The (110C) surface is then perpendicular to the \mathbf{b} -axis. The cation vacancies were assigned to tetrahedral sites along the \mathbf{a} -axis parallel to the (110C) surface for valence balance. Two different adsorption sites were studied as indicated in Fig. 1.

At site A, the surface oxygen atom (Brønsted base site, which we denote O_s^A) interacting with the alcohol $-\text{OH}$ hydrogen (H_{ad}) is in the vicinity of a cation vacancy. This is sometimes called “active H-bonding” [1]. At site B, no cation vacancies are around the O_s^B atom interacting with H_{ad} . As previous density-functional calculations have shown no relaxation effects of consequence for surface atoms, excluding the three-coordinated Al [14], the alumina substrate was frozen in all calculations. Only Al atoms on O_h sites were considered to interact with O_{ad} atom since three-coordinated Al practically does not exit on the surface [14,15,20]. The adsorbed molecules were fully relaxed, including their position relative to the surface except for the cases mentioned explicitly. Vibrational frequencies for modes of the adsorbed molecules were computed in the harmonic approximation and scaled by the recommended 0.9761 for PM3 calculations [28].

3. Results and discussion

3.1. Adsorption from the four-center initial orientation

First we studied the adsorption configuration in which the H_{ad} and O_{ad} atoms of the alcohol and the surface adsorption sites (Lewis acid site Al and Brønsted base site O_s) are in approximately the same plane (Fig. 1). The alcohol molecule is placed in close proximity to the surface (with sufficiently short $H_{ad}-O_s$ and $O_{ad}-Al$ distances for strong interactions) and fully relaxed, including its position relative to the surface. The calculated binding energies and structural parameters are listed in Table 1. In all cases (regardless of whether ΔE is positive or negative), the $O_{ad}-H_{ad}$ bond is broken. The H_{ad} atom bonds to the O_s atom, while the O_{ad} atom bonds to the Al atom. The newly formed Al– O_{ad} bond length is 0.183–0.191 nm (see Table 1), close to Al–O bond lengths in bulk γ -alumina [16]. The distances of $H_{ad}-O_s$ bonds formed at adsorption site B are all close to 0.099 nm, which is slightly longer than the $H_{ad}-O_s$ bond lengths at site A ($R(H_{ad}-O_s^B) - R(H_{ad}-O_s^A) \approx 0.004$ nm). All of these bond distances are indicative of a chemisorbed state. This result is consistent with the IR spectra of alcohols adsorbed on alumina [1], which show the formation of surface alkoxide structures.

To test the energy accuracy of PM3 calculations, we performed hybrid calculations on the binding energies at site A using the ONIOM method available

Table 1
Calculated binding energies and bond distances

Adsorbate	ΔE (kcal mol ⁻¹)	d ($H_{ad}-O_s$) (nm)	d ($O_{ad}-Al$) (nm)
Site A			
CH ₃ OH	-71.1	0.095	0.185
C ₂ H ₅ OH	-68.3	0.095	0.186
C ₃ H ₇ OH	-73.0	0.095	0.188
(CH ₃) ₂ CHOH	-58.6	0.095	0.191
Site B			
CH ₃ OH	-7.9	0.098	0.187
C ₂ H ₅ OH	6.5	0.099	0.183
C ₃ H ₇ OH	7.3	0.099	0.183
(CH ₃) ₂ CHOH	19.8	0.099	0.187

$$\Delta E = E(\text{alcohol}/Al_{48}O_{72}) - E(\text{alcohol}) - E(Al_{48}O_{72}).$$

Table 2
Calculated Mulliken charges

Adsorbent	H_{ad}	O_{ad}	C_nH_{2n+1}	Δe_{mol}	O_s^A	O_s^B
CH ₃ OH						
Free	0.18	-0.31	0.13	0	-0.58	-0.64
Site A	0.25	-0.54	0.09	-0.20	-0.53	-0.65
Site B	0.25	-0.61	0.12	-0.24	-0.60	-0.41
C ₂ H ₅ OH						
Free	0.18	-0.31	0.13	0	-0.58	-0.64
Site A	0.25	-0.53	0.10	-0.18	-0.53	-0.63
Site B	0.27	-0.58	0.11	-0.20	-0.60	-0.42
C ₃ H ₇ OH						
Free	0.18	-0.31	0.13	0	-0.58	-0.64
Site A	0.25	-0.50	0.07	-0.18	-0.50	-0.65
Site B	0.27	-0.58	0.12	-0.19	-0.61	-0.42
(CH ₃) ₂ CHOH						
Free	0.18	-0.31	0.13	0	-0.58	-0.64
Site A	0.25	-0.51	0.07	-0.19	-0.50	-0.65
Site B	0.27	-0.61	0.13	-0.21	-0.59	-0.42

Free denotes independent un-adsorbed molecule.

in Gaussian 98 [29]. The optimized geometries from our PM3 calculations were used. The “high” layer (region treated at the ab initio level) consisted of the adsorbed molecule and the immediate adsorption sites (an Al₂O₃ cluster closest to the adsorbed molecule), the other atoms were placed into “low” layer (region treated at the semi-empirical level). HF/6-31G(d,p) was employed for the high layer, while PM3 was used for the low layer. Four Al and four O atoms in the low layer bound to Al₂O₃ in the high layer were replaced by hydrogen atoms during the high-level part of the ONIOM calculations. The calculated binding energies for the adsorption of methanol, ethanol, propanol and isopropanol were 72.2, 70.7, 79.5 and 53.4 kcal mol⁻¹, respectively (see also Table 1). The absolute deviation of PM3 energies from above energies is <6.5 kcal mol⁻¹ (rms deviation 4.4 kcal mol⁻¹ or 5.7%), supporting the validity of the PM3 approximation for this study.

Mulliken population analysis for the alcohol molecules indicates about 0.2e electron transfer from substrate to adsorbate for all cases of alcohol adsorption (Table 2). After dehydrogenation, the O_{ad} atoms become more negatively charged, and this is true to a slightly greater extent in the case of adsorption involving site B. At the same time, the H_{ad} atoms become more positive, and the electron densities of the alkyl

groups also decrease slightly. The O_s atom is less well valence saturated at site A than it is at site B. The variation of charge population on O_s^A is smaller than $0.08e$ when the adsorption occurs at site A. However, the reduction of O_s^B charge population is quite large (about $0.22e$) when the adsorption happens at site B, which is almost equal to the amount transferred to alcohol molecule. Clearly, O_s^B is more nearly valence saturated and more easily donates electrons. At site A, where the O_s atom that reacts with the alcohol molecule is close to an Al vacancy, the energetic benefit from dehydrogenation is much greater. Note from Table 1 that adsorption of methanol to site A releases an extra 63 kcal mol^{-1} compared to adsorption at site B. For the other alcohols, the interaction with site B is endothermic. The calculated $H_{ad}-O_s$ stretching vibrational frequencies at adsorption site A are in the range of $3683\text{--}3725 \text{ cm}^{-1}$ (O_s is shared by a six- and a four-coordinated O_h Al atom), very close to the range of $3700\text{--}3750 \text{ cm}^{-1}$ assigned to OH groups shared by an octahedrally and a tetrahedrally coordinated Al^{3+} cation [17,30]. On site B, the calculated frequencies of $H_{ad}-O_s$ stretching mode is $3368\text{--}3437 \text{ cm}^{-1}$, inconsistent with measurements ($3635\text{--}3700 \text{ cm}^{-1}$) for three-coordinated oxygen [30], implying that the population of OH groups at site B may be too small to be measured. Together with the binding energies, these results indicate that site B is less favorable than site A for alcohol dehydrogenation.

To see if there is an energy barrier for an alcohol molecule to approach the surface closely enough for dehydrogenation, the adsorption on site A was examined in more detail. The O_{ad} atom of the alcohol molecule was constrained to lie above the surface along a normal vector passing through the midpoint of the $Al-O_s$ bond (the configuration is similar to Fig. 1a). The position of the O_{ad} atom was fixed at different heights ($Al-O_{ad}$ distance varied from about 0.180 to 0.235 nm, in steps of approximately 0.005 nm) and all the other atoms of molecule were relaxed. It is found that once the $Al-O_{ad}$ distance exceeds 0.200 nm, optimization does not proceed to a dehydrogenated state. As shown in Fig. 2, the energy variations with $Al-O_{ad}$ distance before reaction increase with decreasing $Al-O_{ad}$ distance. The energy increase for a free molecule to come to such a surface position with $d(Al-O_{ad}) = 0.200 \text{ nm}$ ($d(O_s-H_{ad})$ is about 0.140 nm) is 36.7, 38.3, 40.7 and $45.7 \text{ kcal mol}^{-1}$

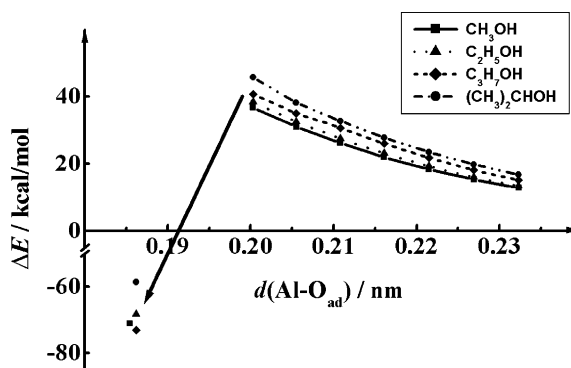


Fig. 2. Energy variations with $Al-O_{ad}$ distance for four simple alcohols. The chemisorbed states are also marked for reference.

for CH_3OH , C_2H_5OH , C_3H_7OH and $(CH_3)_2CHOH$, respectively, which implies that there is an energy barrier to overcome before the chemisorbed state, where dehydrogenation occurs, is accessed. Clearly, the energy barrier increases with increasing molecular size. Based on the computed energy barriers we may estimate the temperature at which the reaction half-life $T_\tau = 1 \text{ h}$. We find that this temperature falls in the range $451 \text{ K} < T_\tau < 563 \text{ K}$ for the species studied. This is in reasonable agreement with experimental observations ($436\text{--}493 \text{ K}$) for the production of ethers from alcohols [6]. Preliminary calculations indicate that zero point vibrational energies (ZPE) are larger for the reactant molecules than for the transition state species. We would therefore expect improved agreement if ZPE were included in the calculations. We would also expect decreased barrier heights with a more complete multi-configuration description of wavefunction, which would more properly describe bond breaking and formation. Such calculations are beyond the scope of this investigation.

3.2. Adsorption from the active H-bonding initial orientation

If the $O_{ad}-H_{ad}$ bond of the alcohol is almost perpendicular to the surface (with H_{ad} closer to the surface than O_{ad}), it is found that upon structural relaxation, dehydrogenation happens at site A when the O_s-H_{ad} distance in the initial configuration is shorter than 0.130 nm . The energy barriers are higher than those described above, where the alcohol was initially

oriented with the OH group in the four-center orientation. Chemisorption at site B does not occur at all from the perpendicular initial orientation, even if the starting O_s-H_{ad} distance is as short as 0.09 nm. Therefore, the involvement of the Lewis acid site is much more important for dehydrogenation at site B. Only at site A, where the basicity of the Brønsted base site is greater due to the existence of a nearby vacancy, may dehydrogenation occur without the involvement of the adjacent Lewis acid site. Involvement of the adjacent Lewis acid site does decrease the energy barrier to reaction, however.

3.3. Alkoxide and alkene formation

According to the Peri model, there are two possible routes for the formation of alkoxide, determined by whether the O–H or C–O bond in the alcohol is broken [1]. This hypothesis is supported by TPD experiments for methanol and ethanol [6]. To see how alkoxide is formed by breaking the C–O bond, adsorption of methanol at site A was studied in a configuration with C instead of H_{ad} close to the surface O_s site. The initial O_{ad} –Al distance was smaller than 0.200 nm. The optimized structure shows that the C– O_{ad} bond does not break in this situation (optimized C– O_{ad} distance 0.139 nm), although a C– O_s bond is formed (0.146 nm). In addition, as two H atoms of the CH_3 group are close to O_s atoms in the initial configuration, one of them is eliminated from CH_3 . Therefore, our results support formation of alkoxide by cleavage of the hydroxyl proton. Since hydroxide itself is a relatively poor leaving group, a secondary interaction of the alcohol hydroxyl with an adjacent acid site may be required besides C– O_s interaction in order to form alkoxide by breaking the C– O_{ad} bond, as proposed by DeCanio et al. [6].

It has been suggested that the dissociation of a surface alkoxide yields olefin [1]. To verify this, the C_3H_7O produced from propanol adsorption on site A with O_{ad} linking to a surface Al site was rotated around O_{ad} , so that one of the H_β atoms was close to a surface O_s site. Upon optimization of this rotated structure the H_β – C_β bond is broken and the H_β atom bonds to the nearby O_s atom. However, the C_α – O_{ad} bond is not influenced and the O_{ad} atom remains bound to a surface Al atom. Increasing reaction temperature may break the O_{ad} –Al bond and form propene [1].

3.4. The influence of interactions

As surface coverage of adsorbed alcohol molecules increases, adjacent molecules may start to interact. To investigate the potential role of such interactions, calculations were carried out for adjacent ethanol molecules. If two C_2H_5OH molecules lie on adjacent A sites with nearly parallel OH bonds (their orientation similar to Fig. 1a), both of them are dehydrogenated. If one molecule (mol 1) is close to the surface with a short H_{ad1} – O_s distance, the other

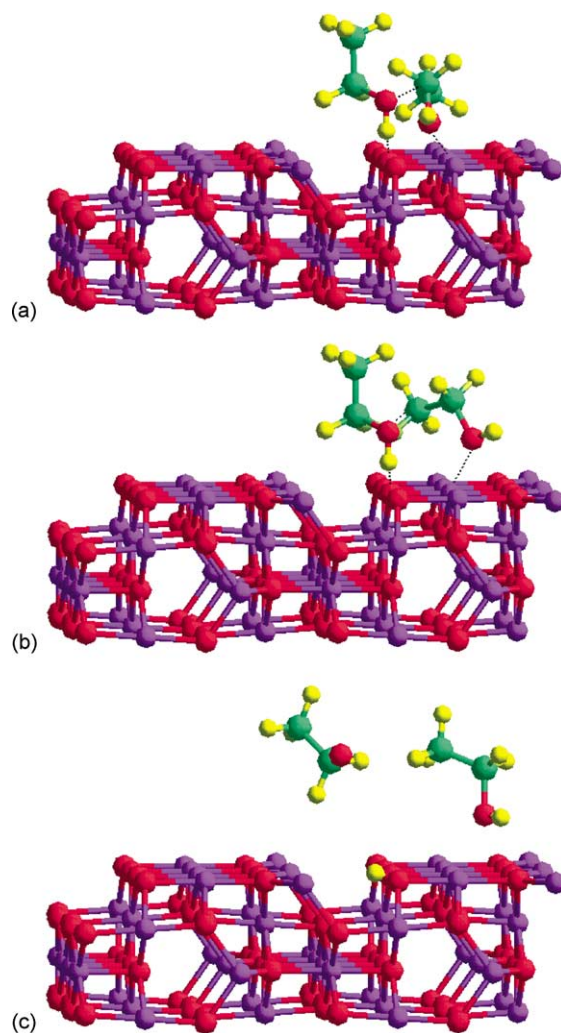


Fig. 3. Adsorption of two ethanol molecules at neighboring sites: (a) and (b) different initial configurations; (c) optimized configuration.

molecule (mol 2) is close to the surface with a short Al–O_{ad2} distance, and the distance of O_{ad1}–C_{ad2} (CH₂ group, Fig. 3a) or O_{ad1}–H_{ad2} (CH₃ group, Fig. 3b) between two molecules is comparable to a normal bond length, only the former molecule is dehydrogenated and the two molecules repel each other (Fig. 3c). This result suggests that the initial configuration of alcohol molecule above substrate is important for the occurrence of dehydrogenation at a Lewis acid site. H_{ad} must have the opportunity to come close to O_s. As O_{ad1} lies on top of O_s after H_{ad1} leaves the OH group of ethanol, the repulsive interaction between O_{ad1} and O_s makes the remaining C₂H₅O fragment move away from the surface. This result implies that the repulsive interaction of the adsorbed molecules with the adjacent ones may block the latter from achieving the critical configuration for dehydrogenation.

4. Conclusions

In conclusion, we have employed semi-empirical (PM3) cluster calculations to investigate the adsorption of several simple alcohols on the γ -alumina (110C) surface. The results show that all four alcohols considered chemisorb to the alumina surface when they come sufficiently close to surface with suitable orientation. The chemisorption is an exothermic process at site A (surface O with adjacent Al vacancy), and only O_s–H_{ad} interaction is required for successful dehydrogenation. At site B (surface O with no adjacent vacancies), both O_s–H_{ad} and O_{ad}–Al interactions are required for successful dehydrogenation, that is, both the alcohol oxygen and hydrogen must interact with the surface. Calculations to investigate the interaction of two molecules at adjacent sites further verify this conclusion. This multi-point interaction means that one adsorbed molecule may block its neighbor from forming the four-center chemisorbed state required for dehydrogenation, implying that dehydrogenation is <100% efficient for high surface coverage. The site preference can be understood in terms of the alcohol hydrogen completing the valence of a surface O_s. The alcohol is acting as a Brønsted acid. Surface O_s atoms with adjacent vacancies serve as stronger Brønsted bases than those with no adjacent vacancies, hence the stronger interaction at site A. The formation of alkoxide by abstraction

of the alcohol OH proton is favored over alkoxide production through C–OH bond scission.

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