The electronic states and Lewis acidity of surface aluminum atoms in γ-Al$_2$O$_3$ model cluster: An *ab initio* MO study

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Abstract

The electronic states of the surface and bulk aluminum ions in γ-Al$_2$O$_3$ have been determined by using *ab initio* molecular orbital (MO) method. As bulk and surface models of γ-Al$_2$O$_3$, $[\text{Al(OH)}_n]^{3-n}$ and $[\text{Al(OH)}_{n-1}]^{4-n}$ ($n=4, 6$) clusters for one-unit model and $[\text{Al}_2\text{O(OH)}_m]^{4-m}$ and $[\text{Al}_2\text{O(OH)}_{m-2}]^{6-m}$ ($m=6, 10$) clusters for two-unit model are chosen. Lewis Acidity of central aluminum ion in each model cluster is characterized by means of both electron density on Al and the energy level of the lowest unoccupied MO (LUMO). Geometry optimization of the model cluster leads to the conclusion that reactivity of surface aluminum is governed by the location of Al relative to oxygen layer as well as the electronic state of surface Al site.

Keywords: Aluminium; Electronic states; Lewis acidity; Molecular orbital study; Surface

1. Introduction

Transition aluminas, such as γ- and η-Al$_2$O$_3$, are widely used as adsorbents, catalysts and catalyst carriers. Compared with γ- and η-Al$_2$O$_3$, α-Al$_2$O$_3$ is less active as a solid acid catalyst. The low activity has been considered so far to be due to its high crystallinity and low surface area (<10 m^2/g). Recently, Tsuchida [1] prepared high surface area α-Al$_2$O$_3$ (66.2 m^2/g) by the thermal decomposition of synthetic diaspore (β-Al$_2$O$_3 \cdot$ H$_2$O) at 530°C, but the alumina thus prepared did not show any catalytic activity for isomerization of 1-butene. This result strongly suggests that the electronic state of surface Al atom, correlating to Lewis acidity of alumina, is a dominant factor in the reactivity rather than the surface area.

Relationship between Lewis acidity and the coordination number of Al^{3+} ion to oxygen ions has been studied experimentally and theoretically [2–5]. Zecchina et al. [2] have made infrared (IR) spectroscopic study on CO molecules adsorbed on γ-Al$_2$O$_3$ surface, and showed that Lewis acidity of the tetrahedral surface Al sites (Al$_{stet}$) with coordination number 3 is much stronger than that of the octahedral surface Al sites (Al$_{soct}$) with coordination number 5. It is experimentally known that the bulk of γ-Al$_2$O$_3$ is composed of both the tetrahedral and octahedral Al sites, whereas that of α-Al$_2$O$_3$ is composed of only the octahedral Al sites.

Recently, Fleisher et al. [3] performed the semi-empirical CNDO/2 molecular orbital (MO) calculation on the cluster models of alumina. The Lewis acidity of the model clusters was charac-

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terized by the charge on Al and the energy level of the lowest unoccupied MO (LUMO).

In the present investigation, the electronic states of surface and bulk models of γ-Al$_2$O$_3$ are determined by means of *ab initio* MO method, which is more quantitative and reliable theory rather than CNDO/2 method. The primary aims of the present study are (i) to elucidate the origin of the lower Lewis acidity of Al$_{soct}$ site than Al$_{stet}$ one and (ii) to estimate interaction energies between these Al sites and NH$_3$.

2. Method of the calculations

2.1. Cluster models

The cluster model approximation is usually used in MO calculations and the tight-binding calculations of solid surface [6]. Therefore in the present work, the approximation is employed to express the surface and bulk of γ-Al$_2$O$_3$. As struc-
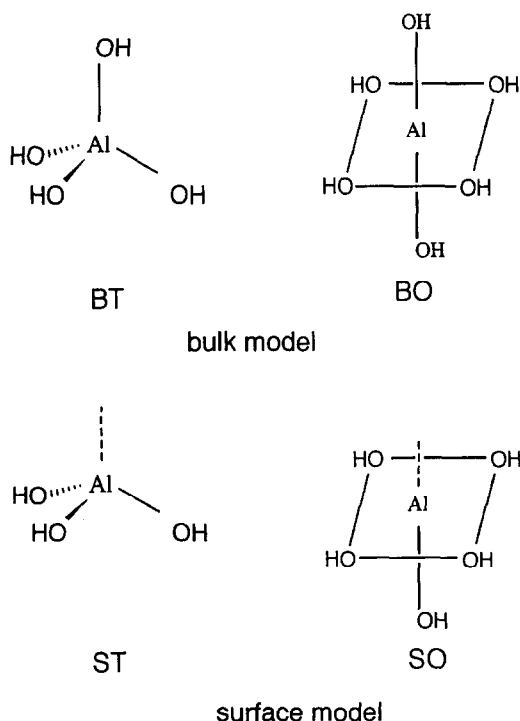

bulk model

surface model

Fig. 1. Cluster models used in ab initio MO calculation.

tural models of γ-Al$_2$O$_3$, [Al(OH)$_n$]$^{3-n}$ and [Al(OH)$_{n-1}$]$^{4-n}$ ($n=4$, 6) clusters are chosen. The former and the latter clusters correspond to the bulk and surface models of γ-Al$_2$O$_3$, respectively. To test cluster size dependency, two-unit models, [Al$_2$O(OH)$_m$]$^{4-m}$ and [Al$_2$O(OH)$_{m-2}$]$^{6-m}$ ($m=6$, 10) clusters are also employed. Schematic representation of the models is shown in Fig. 1. The notations, BT, BO, ST and SO indicate the tetrahedral bulk model, the octahedral bulk model, tetrahedral surface model and octahedral surface model, respectively. The notations, BT2, BO2, ST2 and SO2 indicate two-unit models.

3. Ab initio MO calculation

MO theory has provided valuable information on the structure and electronic states of unstable and stable molecules [6,7]. Hence all calculations are performed at the ab initio MO level. Minimal (STO-3G) and split-valence type (3-21G) bases functions [8] are used for basis sets. Geometries of the model clusters are fully optimized by using the energy gradient method [9]. Electron correlation in the total energy is evaluated by means of Møller–Plesset second order perturbation (MP2) method at each optimized geometry. All *ab initio* MO calculations are performed with GAUSSIAN86 program package [10] on an S-820 super computer.

4. Results and discussion

4.1. Bulk structure of γ-Al$_2$O$_3$

Optimized geometries for BT, BO, BT2 and BO2 are listed in Table 1. Two independent calculations (HF/STO-3G and HF/3-21G) give similar geometries. The optimized Al–O distances for the one-unit models are 1.7505 Å for BT and 1.944 Å for BO and ones for the two-unit models are 1.7942 Å and 1.9898 Å for BO2, indicating that the Al–O bond distance in bulk increases with

Table 1
Optimized geometrical parameters calculated at the HF/3-21G and HF/STO-3G levels for the tetrahedral- and octahedral-bulk models (BT, BO, BT2 and BO2). Bond lengths are in Å and angles are in degrees. HF/STO-3G values are shown in parenthesis

	One-unit model		Two-unit model	
	BT [a]	BO [b]	BT2 [c]	BO2 [d]
r(Al–O)	1.7505 (1.7274)	1.944 (1.8804)	1.7942	1.9898
r(Al–O_c)[e]			1.6915	2.2572
r(O–H)	0.9608 (0.9925)	0.9803 (1.0108)	0.9681	0.9829
∠O–Al–O	109.28 (109.03)	90.0 (90.0)	113.83	90.0
∠Al–O–H	124.97 (106.05)	102.35(107.44)	115.96	104.41

[a] Tetrahedral bulk model (one unit model).
[b] Octahedral bulk model (one unit model).
[c] Tetrahedral bulk model (two unit model).
[d] Octahedral bulk model (two unit model).
[e] O_c = centrate oxygen atom in two unit model.

increasing coordination number of Al. These features are in excellent agreement with the result derived from X-ray experiment [11]. This agreement indicates that the level of theory used in the present work is reasonable for investigating the Al_2O_3 system.

4.2. Surface structure of γ-Al_2O_3

In order to determine the surface structure, the locations of Al relative to oxygen layer are optimized by the energy gradient method. The geometries of oxygen and hydrogen in the model clusters except the centered aluminium ion, are fixed to those of the bulk model. Optimized distances for ST and SO are given in Table 2. ΔZ and Δh are, respectively, the distorted distance of Al from the unrelaxed position and the optimized distance from oxygen layer. As shown in Table 2, ΔZ's for all surface cluster models (ST, SO ST2 and SO2) have negative values. Δh's are

+ 0.2858 Å for ST, − 0.2480 Å for SO, 0.2408 Å for ST2 and − 0.2609 Å for SO2, respectively. These results indicate that the aluminium ion locates over the oxygen layer in the tetrahedral site (ST and ST2) whereas locates under the oxygen layer in octahedral site (SO and SO2). This geometrical deformation of SO strongly affects the surface reactivity of Al_2O_3 as a steric hindrance, as will be discussed in a later section.

4.3. Electronic states of bulk and surface Al site

4.3.1. Charge distribution on Al site

Charges on aluminium and oxygen atoms of the cluster models are summarized in Table 3. In the bulk model, the charges of Al_{btet} and Al_{boct} are + 1.428 and + 1.202, respectively, indicating that Al_{btet} is more ionic than Al_{boct}. This difference becomes larger in the surface model (+ 1.549 for Al_{stet} vs. + 1.210 for Al_{soct}). The bond populations of Al–O imply that Al ion in the tetrahedral cluster

Table 2
Optimized distances (Å) of Al^{3+} ion from unrelaxed position (ΔZ) and from the oxygen layer (Δh). The values are calculated at the HF/3-21G level. Z-direction corresponds to the moleculer axis (C_3-axis for ST and ST2, and C_4-axis for SO and SO2). The HF/STO-3G values are given in parenthesis

	One-unit model		Two-unit model	
	ST	SO	ST2	SO2
ΔZ	− 0.2923 (− 0.3611)	− 0.2480 (− 0.1748)	− 0.2404	− 0.2609
Δh	0.2858 (+ 0.2023)	− 0.2480 (− 0.1748)	0.2819	− 0.2609

Table 3
Charges on Al and O atoms and bond populations of Al–O bond calculated at the HF/3-21G level

	Tetrahedral			Octahedral		
	Bulk (BT)	Surface (SO)		Bulk (BO)	Surface (SO)	
		unrelaxed	relaxed		unrelaxed	relaxed
Al	+ 1.428	+ 1.576	+ 1.549	+ 1.202	+ 1.118	+ 1.210
O	− 0.929	− 0.924	− 0.909	− 0.915	− 0.819	− 0.858
Al–O	0.224	0.255	0.254	0.211	0.222	0.217

connects more covalently with oxygen ion than that in octahedral clusters. As shown in Table 4, the same tendency is seen in case of two-unit models.

4.3.2. Molecular orbital energies

As pointed out by Fleisher et al. [3] and Kawakami and Yoshida [5], the position (depth) of acceptor level localized on the metal ion is one of important parameters of Lewis acidity. The orbital energies of HOMO and LUMO in the model clusters are shown in Fig. 2. The zero-levels of the orbital energy are normalized by the orbital energies of each bulk cluster. By removing a surface OH group from the bulk clusters (BO and BT), both HOMO and LUMO energies are decreased. The energy level of ST is slightly lower than that of SO. Therefore, Al_{stet} acts as a stronger

electron acceptor than Al_{soct}. This feature also supports high acidity of tetrahedral surface Al site.

4.4. Interaction between the surface Al site and NH_3 molecule

In order to test Lewis acidity of Al sites of ST and SO, the interaction with ammonia molecule is studied theoretically. The potential energy curves (PECs) are plotted in Fig. 3 as a function of Al–N distance, $r(Al–N)$. Each PEC has an energy minimum, suggesting that the NH_3 molecule can be bounded to both Al sites (Al_{stet} and Al_{soct}) with the binding energy (ΔE). However, ΔE and bond distance are much difference each other. In the case of bonding to the tetrahedral Al site (ST–NH_3 system), ΔE is obtained to be 56 kcal/mol whereas ΔE in the octahedral site is only
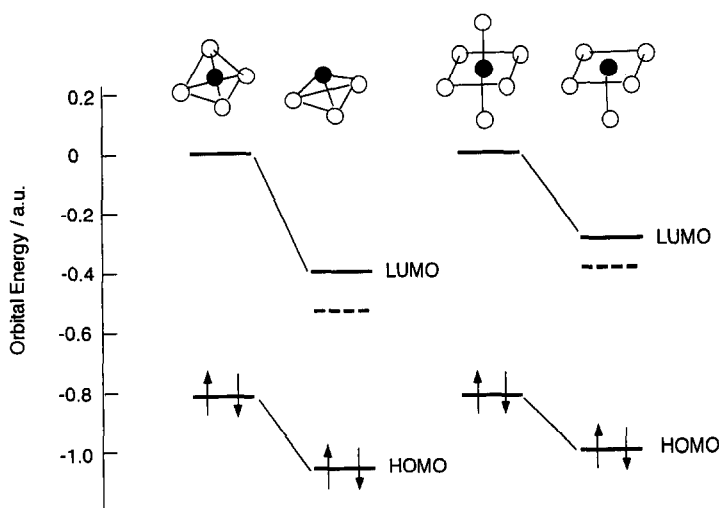

Fig. 2. Orbital energies calculated at the HF/3-21G level. Dashed lines indicate the energy level after geometry optimization.

2 kcal/mol (SO–NH$_3$ system). The bond distance in SO–NH$_3$ system (2.30 Å) is much longer than in ST–NH$_3$ system (2.00 Å). This difference is caused by a steric hindrance between NH$_3$ and surface oxygen ion in SO cluster model. Charges of adsorbed NH$_3$ molecule are calculated to be +0.19 e for ST–NH$_3$ system and +0.01 e for SO–NH$_3$ system, suggesting that the degree of the charge transfer from NH$_3$ to the surface Al site is much larger in ST–NH$_3$ system. This suggests that the tetrahedral surface Al site (Al$_{stet}$) has a stronger Lewis acidity than the octahedral one (Al$_{soct}$).
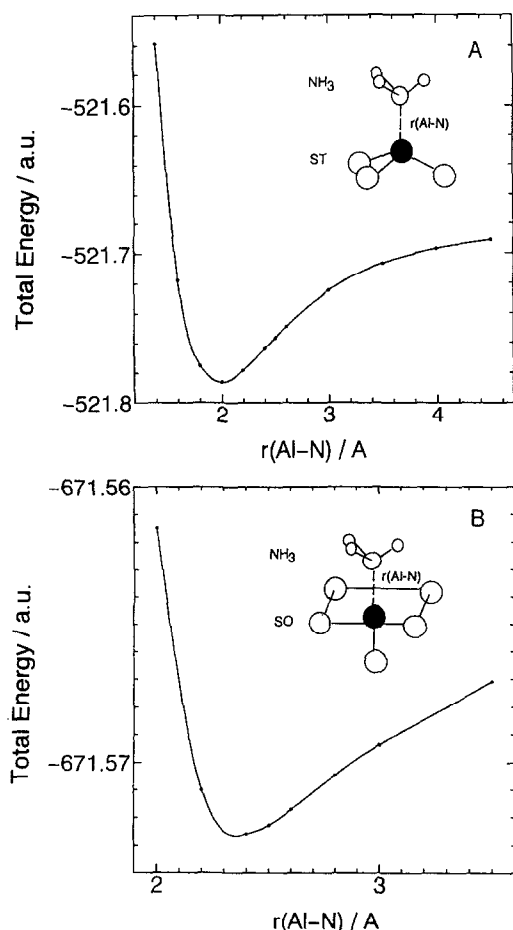
5. Conclusion

In the present work, *ab initio* MO calculations are performed to elucidate Lewis acidity of Al site using the cluster models, $[Al(OH)_n]^{3-n}$, $[Al(OH)_{n-1}]^{4-n}$ ($n=4, 6$), $[Al_2O(OH)_m]^{4-m}$ and $[Al_2O(OH)_{m-2}]^{6-m}$ clusters ($m=6, 10$). The α- and γ-Al$_2$O$_3$ are represented by the octahedral and tetrahedral cluster models, respectively. All calculations show that the tetrahedral surface site (Al$_{stet}$) is more favored as Lewis acidity site. The surface Al atom in octahedral site locates below surface oxygen layer. This structural deformation causes a steric hindrance in an interaction with NH$_3$ molecule. The surface Al atom in the tetrahedral site has little steric hindrance because it locates above the oxygen layer. Thus the steric factor elucidates the low activity of octahedral surface Al site as well as the electronic state.

Acknowledgements

Fig. 3. Potential energy curves calculated as a function of r(Al–N) distance. (A) ST–NH$_3$ system, (B) SO–NH$_3$ system. Values are calculated at the HF/3-21G level.

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