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An ab initio study on formation and desorption reactions of H_2O molecules from surface hydroxyl groups in silicates

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Abstract

Effects of the Al atom on the formation and desorption reactions of H_2O molecules from surface hydroxyl groups in silicates have been investigated by ab initio molecular calculations for $Si(OH)_4$ and $(HO)_3Si(OH)Al(OH)_3$ cluster models. The analysis of the potential energy profiles for the reactions of surface hydroxyls shows that the H_2O complex formation and the H_2O desorption through the interaction of the surface hydroxyls with $Al(OH)_3$ units yield relatively low activation energies. The low energies of these reactions are closely connected with the changes of geometrical parameters and charge distributions caused by the interaction of the surface hydroxyls with $Al(OH)_3$ units. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Tritium release is an important performance of ceramic tritum breeding materials such as lithium silicate and lithium titanate in a fusion reactor. Some improvements of these materials have been done to enhance the low-temperature tritium release [1,2]. The tritium generated by the $^6Li(n,\alpha)^3H$ reactions mainly exist as hydroxyls on the surface of breeding materials [3,4]. The surface hydroxyls play an important role in the tritium release behavior from the solid breeder materials.

Addition of other elements, such as Al, Mg, etc., to the breeding materials is one of several factors influencing the properties of the surface hydroxyls [1,2]. Addition of Al atoms to the lithium silicate improves the tritium release performance at low temperatures. We have investigated the influence of trivalent elements, such as B, Al, and Ga, on the properties of surface hydroxyls in lithium silicate by ab initio molecular orbital calculations [5,6]. It has been confirmed that the interaction of the trivalent elements with the surface hydroxyls increases the ionicity of surface hydrogen, and decreases the deprotonation energy. Especially, the direct interaction of Al atom with the surface hydroxyl induces the largest ionicity of surface hydrogen among B, Al, and Ga atoms.

The aim of the present study is to investigate the effect of the Al atoms on the formation and desorption reactions of the H_2O molecules from the geminal surface hydroxyl in silicates.

2. Models and methods

2.1. Models

Fig. 1 shows local surface structures of silicate glasses that are formed in pure and Al-doped lithium silicates with the sudden changes caused due to an irradiation and a rapid cooling [7–9]. The $Si(OH)_4$ cluster model represents the local structure of silicate glass formed in silicate. The $(HO)_3Si(OH)Al(OH)_3$ cluster model is used to simulate the effect of Al atom doped in silicate glass.

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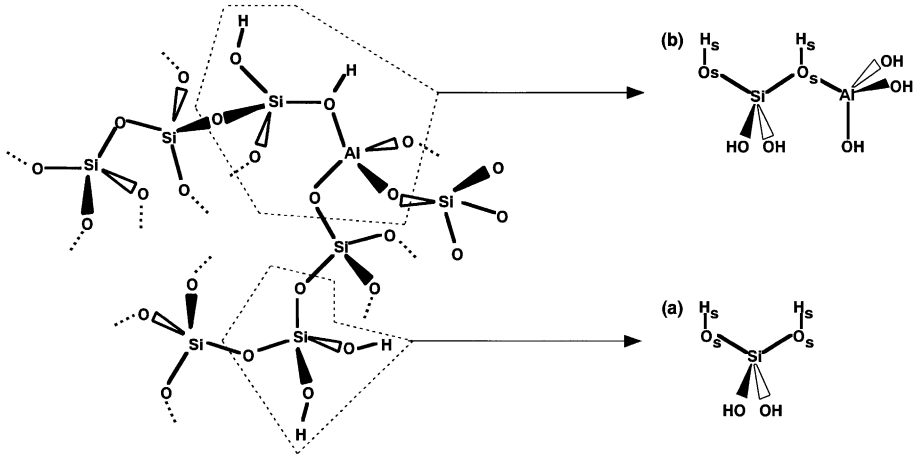

Fig. 1. Structural schemes of geminal surface hydroxyl groups in: (a) silicate glass; (b) silicate glass containing A1 atom.

The $Si(OH)_4$ molecule has been considered as a model for both isolated and geminal types of surface hydroxyls in silica [10,11]. The $(HO)_3Si(OH)Al(OH)_3$ molecule has been used for understanding the chemical property of hydroxyl on aluminosilicate mineral [12].

In the cluster models, H_s and O_s represent the surface hydrogen and oxygen atoms, respectively. Other hydrogen atoms, called 'terminators', in the cluster models are used to saturate the dangling bonds of 'surface' oxygen atoms. It has been shown that such hydrogen terminators do not substantially affect the nature of the Si–O bond [13]. The oxygen atoms terminated by hydrogens can be considered as the bridging oxygen atoms.

2.2. Calculation methods

The Gaussian 94 program [14] is used to carry out all ab initio calculations presented here. The theoretical calculations are based on ab initio molecular orbital theory using Hartree–Fock and Møller–Plesset perturbation theories [15,16]. The electron correlation corrections are limited to the MP2 level. The MP2 method has been shown to account for typically 85–95% of the correlation energy in reasonable computational time [17]. The basis sets used here are the standard 6-31G** basis sets implemented in the Gaussian 94 program, which have p- and d-type polarization functions for the hydrogen and heavy atoms (Si, Al and O), respectively.

All geometrical parameters are fully optimized without assuming symmetry on the structure. The vibrational frequencies are calculated using analytical second derivatives of the total energy. The transition states reported here are confirmed to have one imaginary frequency. The unscaled frequencies are used in the calculations for the vibrational zero-point energy (ZPE) correction. The intrinsic reaction coordinates (IRC) are calculated in order to check and obtain energy profiles of the reactions discussed here [18,19]. The natural atomic charges are computed using the natural bond orbital (NBO) analysis [20–23].

3. Results and discussions

3.1. Geometrices

The formation and desorption of an H_2O molecule from the geminal surface hydroxyl groups ($-O_1H_1$, $-O_2H_2$) simulated by the $Si(HO)_4$ cluster are presented in Fig. 2. The influence of the $Al(OH)_3$ unit on the formation and desorption of an H_2O molecule is simulated by the $(OH)_3Si(OH)Al(OH)_3$ cluster (see Fig. 3). In both the models, the formed H_2O molecule is adsorbed on the isolated cluster, and takes the form of H_2O complex at the first stage. Important bond distances and angles of these structures obtained with no constraints at the HF/6-31G** and MP2/6-31G** levels are shown in Tables 1 and 2, respectively. The natural atomic charges on the most significant atoms are also listed in the above tables.

The geometrical parameters calculated for the $Si(OH)_4$ and $(HO)_3Si(OH)Al(OH)_3$ clusters as the reactants can be compared to the experimental and theoretical values reported previously. The Si–O bond lengths calculated at the HF and MP2 levels for the $Si(OH)_4$ reactant cluster are in good agreement with the experimental values of 1.637 Å for cyclohexylsilanetriol ($C_6H_{11}Si(OH)_3$) [24] and of 1.67 Å for isolated monosilicate ion [$SiO_3(OH)_3^-$] in $NaCaSiO_3(OH)$ [25]. Our calculated values of Si–O and O–H bond lengths and ∠OSiO bond angle for the $Si(OH)_4$ reactant cluster are also in good agreement with the calculations by Kassab [26] at the HF/6-31G level (Si–O = 1.625 Å, O–H = 0.93 Å and ∠OSiO = 108.88°). The geometrical parameters

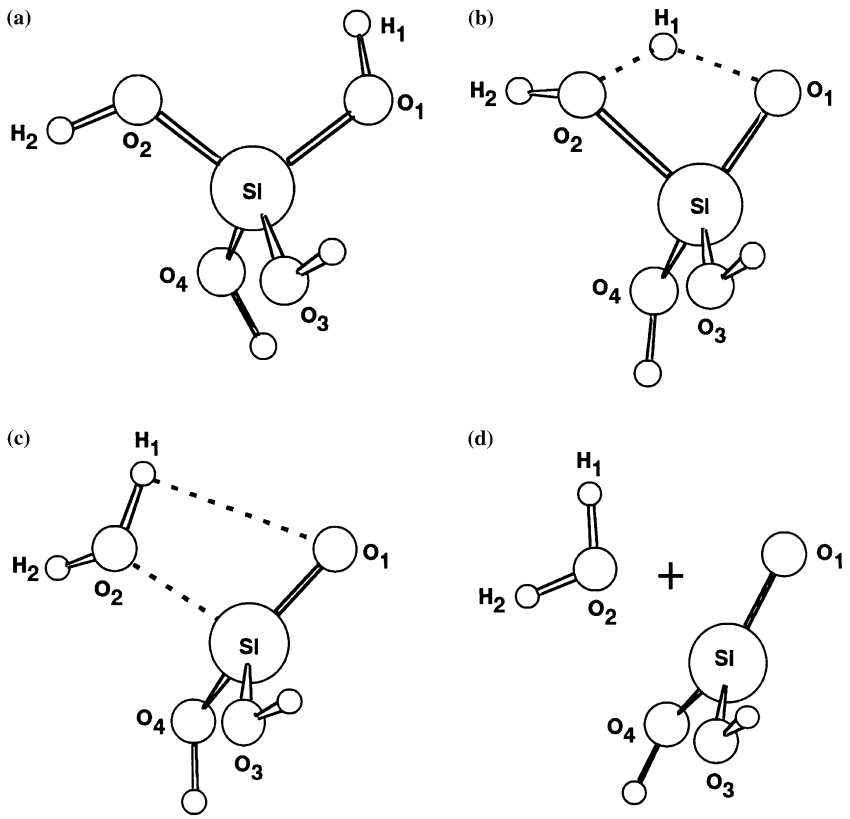

Fig. 2. Optimized structures (MP2/6-31G**) and atom labels for the H_2O formation and desorption reactions from geminal surface hydroxyl in silicate glass: (a) geminal surface hydroxyl; (b) transition state; (c) H_2O complex; (d) H_2O and dehydrated clusters. Terminating H atoms are unlabeled.

of the $Si(OH)_4$ reactant cluster are consistent with previous experimental and theoretical values.

In the Si(OH)Al moiety of $(HO)_3Si(OH)Al(OH)_3$ reactant cluster, the geometrical parameters calculated here are slightly different from the experimental and theoretical values reported previously for structural information of aluminosilicates [27,28]. The average experimental Si–O and Al–O bond lengths and ∠SiOAl bond angle of pyrope crystal ($Mg_3Al_2Si_3O_{12}$) are 1.635 Å, 1.886 Å and 130.0°, respectively [27]. The corresponding values have been calculated to be 1.66 Å, 1.98 Å and 133.5°, respectively, in the previous theoretical study [28] wherein the cluster structure is constrained to the C_s group. The ∠SiOAl bond angle in the $(HO)_3Si(OH)Al(OH)_3$ reactant cluster optimized here is about 30° smaller than the above experimental and theoretical values of the ∠SiOAl bond angle. The above average experimental values are for the bulk structure. The imposition of the C_s symmetry in the geometry optimization makes the bond lengths and angle of the Si(OH)Al moiety in the $(HO)_3Si(OH)Al(OH)_3$ cluster close to those for the bulk structure. However, the surface structure of aluminosilicates is not always in agreement with the bulk structure estimated by the experimental techniques such as X-ray diffraction which only give the indirect structural information. On the other hand, an unusually high frequency for the streching vibration ν_{OH} of the bridging OH group in amorphous aluminosilicates was observed in the range 3720–3740 cm^{-1} [29]. The high frequency was explained with an unusually small SiOAl angle calculated at 93° by quantum chemical calculations [28], which was very close to the ∠SiOAl bond angle in the $(HO)_3Si(OH)Al(OH)_3$ reactant cluster optimized in this study. The other geometrical parameters presented here are also consistent with those reported. Thus, the Si(OH)Al bridge is considered to take the small SiOAl bond angle in the surface structure of aluminosilicates. Also, the oxygen atom (O_5) of $Al(OH)_3$ unit interacts with the silicon atom by the request of the unusually small SiOAl bond angle.

As stated above, the $(HO)_3Si(OH)Al(OH)_3$ reactant cluster optimized here without symmetry constraint is considered to represent a surface structure of the Si(OH)Al bridge in aluminosilicates. Moreover, all vibrational frequencies for the $(HO)_3Si(OH)Al(OH)_3$

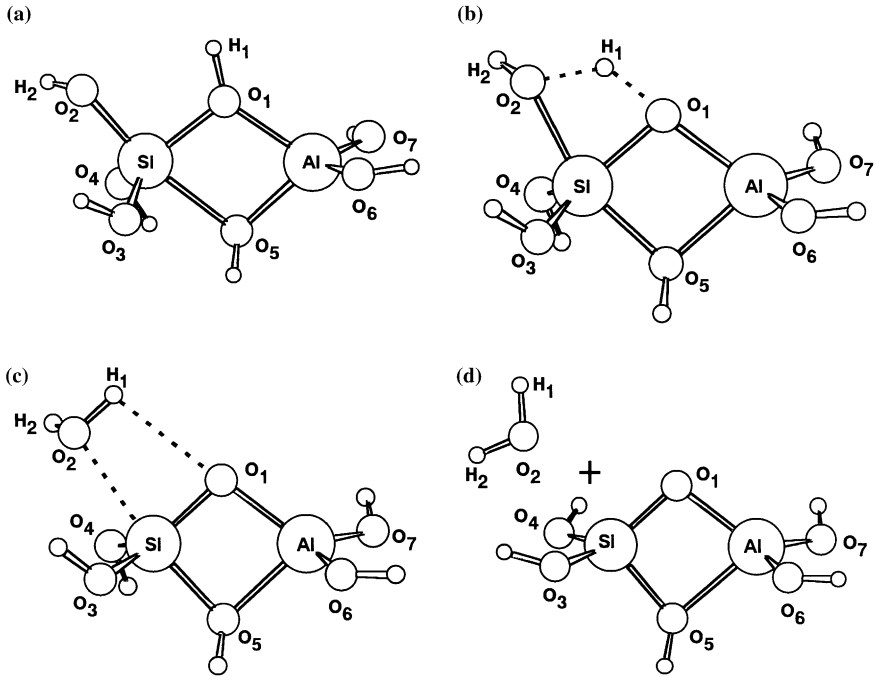

Fig. 3. Optimized structures (MP2/6-31G**) and atom labels for the H_2O formation and desorption reactions from geminal surface hydroxyl in silicate glass containing Al atom: (a) geminal surface hydroxyl interacting with $Al(OH)_3$ unit; (b) transition state; (c) H_2O complex; (d) H_2O and dehydrated clusters. Terminating H atoms are unlabeled.

Table 1
Geometrical parameters and natural charges at HF/6-31G** and MP2/6-31G** levels for reactant, transition state, H_2O complex and products in the H_2O formation and desorption reactions from geminal surface hydroxyl in silicate glass

	Reactant		TS		H_2O complex		Products	
	HF	MP2	FH	MP2	HF	MP2	HF	MP2
Parameters								
d(Si–O_1)	1.628	1.651	1.549	1.576	1.507	1.541	1.490	1.530
d(Si–O_2)	1.628	1.651	1.828	1.887	1.929	1.970	–	–
d(O_1–H_1)	0.942	0.962	1.407	1.478	2.446	2.415	–	–
d(O_2–H_2)	0.942	0.962	0.947	0.969	0.949	0.970	0.943	0.961
$\angle O_1SiO_2$	106.6	106.0	83.8	84.6	98.8	98.5	–	–
Charges								
q(Si)	2.602	2.599	2.561	2.549	2.513	2.504	2.493	2.477
q(O_1)	−1.180	−1.181	−1.318	−1.312	−1.328	−1.316	−1.243	−1.229
q(O_2)	−1.180	−1.181	−1.112	−1.104	−1.002	−1.014	−0.971	−0.974
q(H_1)	0.529	0.531	0.602	0.598	0.569	0.572	0.486	0.487
q(H_2)	0.529	0.531	0.545	0.548	0.557	0.562	0.486	0.487

Geometrical parameters are given in angstroms and degrees.

cluster optimized here are real. That is to say, the $(HO)_3Si(OH)Al(OH)_3$ reactant cluster optimized here corresponds to the true local minimum within the model. By contrast, the C_s symmetry does not provide a true local energy minimum for the $(HO)_3Si(OH)Al(OH)_3$ reactant cluster though the imposition of the symmetry gives the structural information which is correspondent to the bulk structure of aluminosilicates. We confirm that the vibrational analysis yields two imaginary frequencies for the C_s structure of $(HO)_3Si(OH)Al(OH)_3$ cluster. Thus, the C_s symmetry is not taken into the optimization in this study. Our goal is to examine the influence of $Al(OH)_3$ unit on the H_2O formation and desorption from geminal surface

Table 2
Geometrical parameters and natural charges at HF/6-31G** and MP2/6-31G** levels for reactant, transition state, H_2O complex and products in the H_2O formation and desorption reactions from geminal surface hydroxyl in silicate glass containing Al atom

	Reactant		TS		H_2O complex		Products	
	HF	MP2	HF	MP2	HF	MP2	HF	MP2
Parameters								
$d(Si–O_1)$	1.745	1.780	1.693	1.726	1.604	1.640	1.590	1.617
$d(Si–O_2)$	1.669	1.694	1.854	1.868	2.301	2.113	–	–
$d(Al–O_1)$	1.871	1.871	1.809	1.825	1.781	1.807	1.780	1.810
$d(O_1–H_1)$	0.944	0.964	1.195	1.202	2.317	2.135	–	–
$d(O_2–H_2)$	0.942	0.963	0.945	0.973	0.946	0.969	0.943	0.961
$\angle O_1SiO_2$	92.7	91.6	75.9	76.2	82.6	83.8	–	–
$\angle SiO_1Al$	107.2	105.5	102.5	101.1	101.2	99.3	101.3	99.1
Charges								
q(Si)	2.627	2.625	2.612	2.609	2.615	2.600	2.602	2.597
q(Al)	2.151	2.152	2.160	2.160	2.145	2.140	2.151	2.148
$q(O_1)$	−1.215	−1.227	−1.367	−1.366	−1.402	−1.401	−1.380	−1.374
$q(O_2)$	−1.209	−1.210	−1.149	−1.155	−1.007	−1.022	−0.971	−0.974
$q(H_1)$	0.569	0.576	0.622	0.625	0.538	0.561	0.486	0.487
$q(H_2)$	0.521	0.522	0.534	0.538	0.530	0.551	0.486	0.487

Geometrical parameters are given in Ångstroms and degrees.

hydroxyl, but not to resolve detailed structure of bulk equilibrium geometries. Therefore, we adopt the C_1 structure of $(HO)_3Si(OH)Al(OH)_3$ cluster as the reactant in this study. All C_1 structures of clusters computed as reactant, H_2O complex and product models are confirmed to be true local minima.

3.2. Electron correlation effects on structures

The inclusion of electron correlation energy with the MP2 calculation give virtually the same bond lengths and angles as the HF calculation (Tables 1 and 2) in most cases. However, detailed observations of the geometrical parameters show that the MP2 structures have characteristic differences compared with the HF structures with respect to the intermolecular bond distances of the H_2O complexes. Most of intramolecular bond distances become longer by including electron correlation [30], while the intermolecular $O_1–H_1$ bond distances, which are only observed in the H_2O complexes, become somewhat shorter. The intermolecular $Si–O_2$ bond distance in the H_2O complex of the $Si(OH)_4$ cluster is lengthened by the inclusion of electron correlation. On the contrary, the electron correlation yields shorter intermolecular $Si–O_2$ bond distance in the H_2O complex of $(HO)_3Si(OH)Al(OH)_3$ cluster.

The inclusion of electron correlation energy yields changes of bond distances as stated above. The lengthening of intramolecular bond distances due to the electron correlation effect is caused by a redistribution of electron density away from bond centers toward the exterior of molecules [30]. The intermolecular $O_1–H_1$ bond distances are curtailed by the inclusion of electron correlation because the correlation yields a stronger interaction by accounting for dispersion effects between the adsorbed H_2O molecule and the isolated cluster model [31]. The change of intermolecular $O_1–H_1$ bond distance is caused by the mechanism different from that of intramolecular bond distance.

The intermolecular $Si–O_2$ bond distances in H_2O complexes of $(HO)_3Si(OH)Al(OH)_3$ cluster, in contrast to the case of the H_2O complex of $Si(OH)_4$ cluster, are shortened by the effect of electron correlation. The reason for the shortening of the intermolecular $Si–O_2$ bond distance is similar to that of the intermolecular $O_1–H_1$ bond distances in the H_2O complexes. Thus, the different mechanisms are considered to be responsible for the changes of the intermolecular $Si–O_2$ bond distances in H_2O complexes of $(HO)_3Si(OH)Al(OH)_3$ and $Si(OH)_4$ clusters. That is to say, it is expected that the redistribution of electron density has a larger effect on the $Si–O_2$ bond in the H_2O complex of $Si(OH)_4$ cluster than on the $Si–O_2$ bond in the H_2O complex of $(HO)_3Si(OH)Al(OH)_3$ cluster. For the $Si–O_2$ bond in the H_2O complex of $(HO)_3Si(OH)Al(OH)_3$ cluster, the effect of dispersion energy is considered to be superior to that of redistribution of electron density.

3.3. Reaction profiles

Fig. 4 shows the MP2/6-31G** potential energy profiles which correspond to the H_2O formation and desorption reactions from geminal surface hydroxyls in $Si(OH)_4$ and $(HO)_3Si(OH)Al(OH)_3$ clusters. The values in parentheses are the energies calculated at the HF/6-

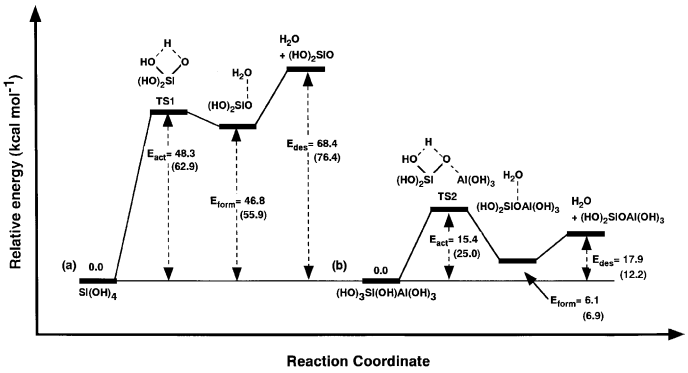

Fig. 4. MP2/6-31G** reaction profiles for the H_2O formation and desorption reactions from geminal surface hydroxyls in: (a) silicate glass; (b) silicate glass containing Al atom. The values in parentheses are calculated at HF/6-31G** level. E_{act} stands for the activation energy, E_{form} the formation energy, and E_{des} the desorption energy.

31G** level. The energies calculated at the MP2 level have larger negative values than those at the HF level because of the electron correlation energy included by MP2 calculation.

The activation energies calculated for the formation of H_2O molecules in $Si(OH)_4$ and $(HO)_3Si(OH)Al(OH)_3$ clusters are 48.3 (62.9) and 15.4 (25.0) kcal/mol, respectively. The H_2O molecules are adsorbed on the isolated clusters to form the H_2O complexes. The formation energies of H_2O complexes in $Si(OH)_4$ and $(HO)_3Si(OH)Al(OH)_3$ clusters are 46.8 (55.9) and 6.1 (6.9) kcal/mol, respectively. The desorption energies of H_2O molecules from the H_2O complexes are 21.6 (20.5) and 11.8 (5.3) kcal/mol, respectively. The desorption energies are calculated as a difference between the sum of the total energies of the H_2O molecule and isolated cluster, and the total energy of the H_2O complex. The reaction energies of the formation and desorption of H_2O molecule in the $Si(OH)_4$ cluster are decreased by the influence of $Al(OH)_3$ unit. The lowering in the activation, H_2O complex formation and H_2O desorption energies due to the interaction are 32.9 (37.9), 40.7 (49.0) and 9.8 (15.2) kcal/mol, respectively. Such energy lowering is related to the influence of the $Al(OH)_3$ unit on the geometrical parameters and charge distributions in the reactants, transition states and H_2O complexes.

At the MP2 level, the $\angle O_1SiO_2$ bond angle in the $Si(OH)_4$ reactant cluster decreases from 106.0° to 91.6° by interaction with the $Al(OH)_3$ unit. The decrease of the $\angle O_1SiO_2$ bond angle causes a shortening of the $O_1 \cdots O_2$ distance. The shortening of the $O_1 \cdots O_2$ distance due to the interaction is also observed in the calculations at the HF level. Thus, the interaction results in a small displacement in the H_1 hydrogen migration to form H_2O molecule.

The $Al(OH)_3$ unit interaction also affects the location of transition state on the reaction coordinate for the hydrogen migration. The geometry of transition state (TS1) structure in the $Si(OH)_4$ cluster is also changed by the interaction with the $Al(OH)_3$ unit. The O_1–H_1 bond distance and $\angle O_1SiO_2$ bond angle in TS1 structure are decreased by the interaction. The scrutiny of the relationships of the geometries, the energies and other properties of TS structures to the overall reaction thermochemistry was carried out using the ab initio molecular orbital calculations [32,33]. The TS1 structure with long O_1–H_1 bond distance is characterized as the late transition state with product-like structure [34,35]. The $(HO)_3Si(OH)Al(OH)_3$ transition state (TS2) structure with short O_1–H_1 bond distance is characterized as the early transition state with reactant-like structure [34,35]. The transition state structures are normally characterized by weak partial bonds, that is, those being broken or formed. A linear relation between the calculated distances of bonds being broken in the transition state structures and the calculated heats of reaction has been found [32,33]. The shorter the distances of bonds being broken in the transition state structures, the smaller the energies of reactions. It is consistent with the above findings in [32,33] that the activation and H_2O complex formation energies calculated for the $(HO)_3Si(OH)Al(OH)_3$ cluster are smaller than that for the $Si(OH)_4$ one.

The energy of the H_2O desorption is substantially depressed by the $Al(OH)_3$ unit interaction. The desorption energies of H_2O molecules from the H_2O complexes are 21.6 (20.5) and 11.8 (5.3) kcal/mol for the $Si(OH)_4$ and $(HO)_3Si(OH)Al(OH)_3$ clusters, respectively. The decrease in the desorption energies due to the interaction in $Al(OH)_3$ unit corresponds to the weaker interaction of H_2O molecules in the H_2O complexes.

The H_2O complexes are found to be stabilized by the Si–O_2 coordination rather than by the hydrogen bond between the H_1 and O_1. The Wiberg bond indices [36] calculated by the NBO analysis indicate that the interaction between oxygen atom, O_2, and Si atom in the

H_2O complexes is significant in the desorption process. The Wiberg bond index is indicative of a bond order. At the MP2 level, the Wiberg bond indices of the $Si\cdots O_1$ and $O_1\cdots H_1$ bonds in the H_2O complex of $Si(OH)_4$ cluster are 0.216 and 0.007, respectively. In the H_2O complex of $(HO)_3Si(OH)Al(OH)_3$ cluster, the bond indices of the $Si\cdots O_2$ and $O_1\cdots H_1$ bonds at the MP2 level are 0.165 and 0.009, respectively. Relative to the values of the bond indices for the $Si\cdots O_2$ bonds, those of the bond indices for the $O_1\cdots H_1$ bonds are extremely small. The value of the bond index for the $Si\cdots O_2$ bond in the H_2O complex of $Si(OH)_4$ cluster is reduced by the interaction with $Al(OH)_3$ unit. The reduction corresponds to that of the desorption energy due to the interaction with $Al(OH)_3$ unit. It is understood from these bond indices that the desorption energies are closely associated with the $Si\cdots O_2$ interaction. The relation of the $Si\cdots O_2$ interaction to the desorption energy can be recognized from bond distances in the H_2O complexes as well as from the Wiberg bond indices. At the MP2 level, the $Si\cdots O_2$ distance increases from 1.970 to 2.113 Å by the interaction of $Al(OH)_3$ unit, while the $O_1\cdots H_1$ distance decreases from 2.415 to 2.135 Å (see Tables 1 and 2). The same tendencies are observed for the $Si\cdots O_2$ and $O_1\cdots H_1$ distances in the calculations at the HF level. The increase of the $Si\cdots O_2$ distance agrees well with the lower interaction energy of the H_2O complex of $(HO)_3Si(OH)Al(OH)_3$ cluster. On the other hand, the decrease of the $O_1\cdots H_1$ distance is inconsistent with that of the desorption energy. If the formed H_2O molecule is adsorbed to the isolated cluster by the $O_1\cdots H_1$ interaction, the desorption energy should become large with the decrease of the $O_1\cdots H_1$ distance due to the interaction. However, the desorption energy of H_2O molecule from the complex is diminished by the interaction. That is to say, the formed H_2O molecule is not adsorbed to the isolated cluster by the $O_1\cdots H_1$ interaction but by the $Si\cdots O_2$ interaction. Consequently, the desorption energies of H_2O molecules from complexes are considered to be mainly connected with the interaction between oxygen atom, O_2, in the adsorbed H_2O molecule and Si atom in the isolated cluster. The $O_1\cdots H_1$ interaction energies in the H_2O complexes should be negligibly small.

The interactions with $Al(OH)_3$ unit have some influences on the charge distributions as well as on the geometries of reactant, transition state, and H_2O complex structures. The MP2 natural charges of surface hydrogen (H_1) in the $Si(OH)_4$ reactant increase from 0.531e to 0.567e by the interaction of $Al(OH)_3$ unit. Such an increase in the ionicity of hydrogen (H_1) results in the decrease of deprotonation energy [5,6]. The increase in the ionicity of hydrogen (H_1) due to the interaction is also maintained for the transition states. The increase in the ionicity of hydrogen (H_1) is also observed for the reactant and transition state structures at the HF level. Thus, the maintaining of the higher ionicity of surface hydrogen due to the interaction with $Al(OH)_3$ unit causes the H_2O formation with the lower activation energy.

The interaction with $Al(OH)_3$ unit affects reaction mechanisms as well as reaction energies for the H_2O formation and desorption from geminal surface hydroxyl in $Si(OH)_4$ reactant cluster. In the H_2O formation and desorption reactions in $Si(OH)_4$ cluster, the energy profile presents that the H_2O desorption energy is larger than the actviation energy for the H_2O formation. This indicates that the overall H_2O desorption rate is controlled by the second-stage H_2O desorption process in $Si(OH)_4$ cluster. On the contrary, the activation energy for the H_2O formation is shown to be larger than the H_2O desorption energy in the energy profile calculated for the $(HO)_3Si(OH)Al(OH)_3$ cluster. The H_2O formation process is indicated to be dominant for the H_2O formation and desorption reactions in $(HO)_3Si(OH)Al(OH)_3$ cluster. Thus, the H_2O desorption and formation reactions are regarded as rate-determining steps of the H_2O release from the $Si(OH)_4$ and $(HO)_3Si(OH)Al(OH)_3$ clusters, respectively. It is found that the direct interaction with $Al(OH)_3$ unit to the surface hydroxyl influences not only reaction energies but also mechanisms for the H_2O formation and desorption reactions.

The reaction energy profiles shown in Fig. 4 are also very useful from the experimental point of view, since the interaction of $Al(OH)_3$ unit with the surface hydroxyl groups are found to play a significant role in the formation and desorption reactions of H_2O molecule on the surface of silicates. It is suggested from the energy profiles that the H_2O formation and desorption reactions should proceed at low temperatures due to the interaction with $Al(OH)_3$ unit. The results obtained in the present calculations are consistent with the experimental results [1] wherein the doping of the Al atom is shown to promote the tritium release from lithium silicate at low temperatures. The outcomes of this study are very useful for the understanding of the tritium release behavior from the Al-doped lithium silicate.

4. Conclusions

From the ab initio study with the HF/6-31G** and MP2/6-31G** methods on the influence of the $Al(OH)_3$ unit on the formation and desorption reactions of H_2O molecules from the geminal surface hydroxyl in silicate glasses, the following conclusions may be drawn.

1. Firstly, the activation, H_2O complex formation and H_2O desorption energies are found to be reduced by the interaction of $Al(OH)_3$ unit with the surface hydroxyls. By the interaction with $Al(OH)_3$ unit, the rate-determining step of the H_2O formation and desorption reactions in $Si(OH)_4$ cluster is shifted

from the H_2O desorption reaction to the H_2O formation one. The $Al(OH)_3$ unit plays a significant role in the formation and desorption reactions of H_2O molecules from the geminal surface hydroxyl in silicate glasses.

2. Secondly, the changes of the geometrical parameters and charge distributions due to the interaction of $Al(OH)_3$ unit, which are observed for the reactants, transition states and H_2O complexes, are directly connected with the reduction of the reaction energies in the formation and desorption of H_2O molecule. The interaction increases the ionicity of surface hydrogen, and decreases the displacement of the displacement of the cluster structure during the H_2O formation.

The results obtained in the present study are very useful to understand the reactions between surface hydroxyls in silicate glasses in the scope of the fundamental understanding of tritium release mechanism.

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