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Ab initio MO study on hydrogen release from surface of lithium silicate

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Abstract

Chemical nature of hydrogen on the lithium silicate and Al-doped lithium silicate surfaces was investigated with ab initio molecular orbital calculations. From the results of calculations, the charge distributions and proton affinity (PA) were obtained for the model clusters $H_{4-x}SiO_4Li_x$ and $H_{7-x}SiAlO_7Li_x$ ($x=0$ and 1). It was shown by the calculation that the ionicity of surface hydrogen is strengthened by the interaction of Al atom to surface oxygen, while weakened by Li ion coordinated to nonbridging oxygen. Also, PA values decrease with increase in the ionicity of the surface hydrogen. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Some ternary lithium ceramics such as lithium orthosilicate are among candidate ceramic tritium breeding materials for fusion blankets. Tritium release is an important characteristic of the breeding materials. Some attempts have been made to enhance the tritium release performance. Doping the other element with different valence is one of the methods to improve the tritium release. It was shown in the study of Vollath et al. that tritium release from lithium orthosilicate was improved by doping Al [1]. Botter et al. also showed by experiment that the low-temperature tritium release was improved by the addition of Mg to lithium aluminate [2]. Matsuyama et al. confirmed by experiment that the doping of 10% Ni to silica and alumina promoted the liberation of tritium gas and the formation of T-compounds [3]. However, it cannot yet be thoroughly understood whether these improvements are due to an increase in diffusion coefficients, a reduction in grain size, or a change of surface structure.

Various changes in these materials are also known to be induced by irradiation. Formation and properties of radiation-induced defects and radiolysis products have been investigated for lithium silicates [4,5]. Recently, we have investigated the formation of Si–O–Si network structure in lithium orthosilicate due to irradiation by infrared spectroscopy and semi-empirical molecular orbital calculation [6]. The network structure is regarded as lithium silicate glass structure.

Tritium release process of ceramic tritium breeding materials consists of many processes, that is, bulk diffusion in the crystal grain, grain boundary diffusions, surface desorption, pore diffusion, etc. The changes due to irradiation affect tritium release performance through the bulk diffusion and the surface desorption processes. In most cases, the surface desorption process is the rate-determining step for tritium release. Therefore, it is important to obtain information about influence of change of lithium silicate surface on the tritium release. In this study, we investigated chemical nature of surface hydrogen atom on lithium silica glass, formed in lithium silicate by irradiation, with ab initio molecular orbital calculation.

2. Models and calculational procedure

Small clusters are employed here to deduce surface properties of lithium silicates (see Fig. 1). These clusters simulate the local network structure formed in lithium silicate and Al-doped lithium silicate by the irradiation. In the model clusters, H_s and O_s represent the surface hydrogen and oxygen atoms, respectively. In the model

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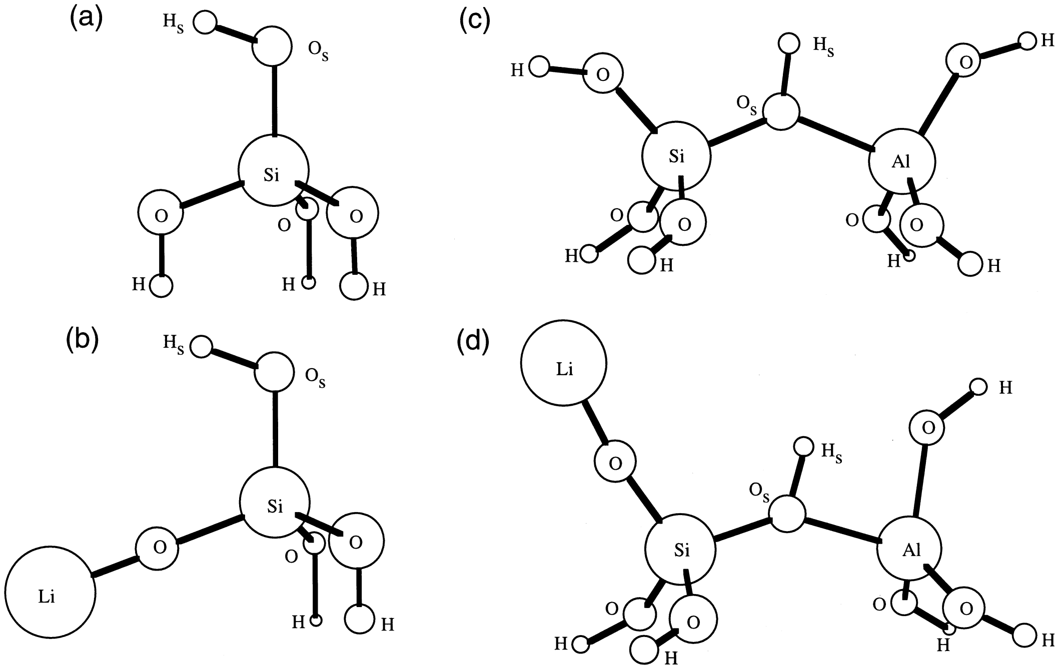

Fig. 1. Clusters modeling the local structure of lithium silicate and Al-doped lithium silicate.

clusters, hydrogen atoms are used to saturate the dangling bonds of “surface” oxygen atoms. It has been suggested that such hydrogen terminators do not affect the nature of Si–O bond [7]. Therefore, the oxygen atoms terminated by hydrogen can be considered as the bridging oxygen atoms energetically. On the other hand, the oxygen atoms adjacent to lithium atoms are regarded as nonbridging oxygen atoms (O_{nb}). The lithium and hydrogen atoms were placed in the respective O_s–Si–O planes. Within this constraint and C_s symmetry we completely optimized the structure of the model clusters.

All ab initio MO calculations were carried out using the Gaussian 94 program [8]. The geometries of clusters were optimized at the Hartree–Fock (HF) level with the STO–3G basis set [9] by means of the gradient method [10]. The HF/STO–3G geometries were used for single-point calculations with the split-valence basis sets such as the 3–21G and 3–21G+ polarization *d* functions on Si,Al and O basis sets. The *d* functions on Si,Al, and O have been established to obtain realistic charge distribution in the clusters containing Si–O or Al–O bonds [11,12]. In this study, the 3–21G basis set augmented by *d* functions on X atom was represented as 3–21G+*d*(X). Atomic charges for the model clusters were obtained from a Mulliken population analysis [13].

The proton affinity (PA) of the model clusters was calculated from the difference in energetics of the protonated (SH) and unprotonated (S^-) clusters

$$PA = E(S^-) - E(SH). \qquad (1)$$

This corresponds to the energy of the reaction

$$SH \rightarrow S^- + H^+ \qquad (2)$$

i.e., the proton affinity of S^- (or, equivalently, the deprotonation energy of SH). Unless noted, the proton affinities calculated did not include zero-point energies.

3. Results and discussions

3.1. Optimized geometry

The optimized parameters of the model clusters at the HF/STO–3G level are listed in Table 1. And also, the experimental values obtained by X-ray scattering method and NMR spectroscopy for various silicates and aluminosilicates are given in Table 2. It can be seen that the calculated Li–O bond lengths are particularly shorter than the corresponding observed bond lengths. These errors for Li–O bond lengths are thought to be due to the minimal STO–3G basis set adopted in this optimization procedure. It has been reported that for bonds between oxygen and electropositive elements such a minimal basis set generally yields bond lengths shorter than experimental values [12]. The calculated Li–O–Si bond angles are larger than the corresponding observed bond angles. Many compounds containing alkali metals such as lithium are known as quasi-structureless molecules [20]. This discrepancy in the Li–O–Si bond angles

Table 1
Optimized geometries of $H_{4-x}SiO_4Li_x$ and $H_{7-x}SiAlO_7Li_x$ at the STO–3G level [a]

	$H_{4-x}SiO_4Li_x$		$H_{7-x}SiAlO_7Li_x$	
	$x=0$	$x=1$	$x=0$	$x=1$
Distances				
Si–O_s	1.657	1.657	1.662	1.674
Si–OH	1.657	1.658	1.653	1.654
Si–O_{nb}		1.620		1.605
Al–O_s			1.835	1.825
Al–OH			1.691	1.693
av Si–O	1.657	1.657	1.655	1.661
av Al–O			1.727	1.726
H_s–O_s	0.983	0.983	0.975	0.974
Li–O_{nb}		1.467		1.475
Angles				
Si–O–Al			134.44	135.96
Si–O_{nb}–Li		179.55		179.08
av O–Si–O	109.47	109.47	109.47	109.47
av O–Al–O			108.04	108.27

[a] Distances in angstroms and angles in degrees.

is considered to be due to the quasi-structurelessness of the system. All of the optimized parameters, except for Li–O bond length and Li–O–Si bond angle, are substantially in good agreement with the experimental values. Therefore, we consider that the structures of small clusters optimized with the STO–3G basis set can simulate the structures of lithium silica glass formed in lithium silicate and Al-doped lithium silicate by irradiation.

3.2. Charge distribution

Atomic charges obtained from a Mulliken population analysis [13] for the model clusters are collected in Table 3. H_4SiO_4 and H_3SiO_4Li clusters correspond to the silica glass structure in lithium silicate formed by irradiation. H_7SiAlO_7 and H_6SiAlO_7Li clusters are considered to simulate the effect of Al atom in the silica glass structure in Al-doped lithium silicate formed by irradiation (see Fig. 1). Atomic charges on each atom are observed to be largely affected by the interaction between the Al and O_s. By the interaction, the positive charges on both H_s and Si atoms become large. The negative charge on O_s also becomes large. The changes of charges can be explained by the charge transfer due to the interaction between Al and O_s [21]. It is also observed that the atomic charges on each atom are affected by the nonbridging oxygen with Li atom. With the existence of a nonbridging oxygen with Li atom, the positive charges on both H_s and Si atoms is small and the negative charge on O_s is large.

From these results, the Li ions that coordinate to nonbridging oxygen atoms are considered to affect the charge distributions of surface atoms. This is known as a "nonlocalized effect of alkali metal ion" [12]. Thus, Li ions affect the electron density of the bridging oxygens and surface hydrogens as well as that of nonbridging oxygens. The effect of Na ions upon the glass structure has been also confirmed by X-ray emission analyses [22].

From results obtained with a Mulliken population analysis, the charge of surface hydrogen in silica glass is considered to be affected by the interaction of Al to surface oxygen and the nonlocalized effect of Li ion.

3.3. Proton affinity

The proton affinities (PA) of the model clusters obtained with Eq. (1) are collected in Table 3. The PA values of H_4SiO_4 and H_7SiAlO_7 clusters are smaller than those of H_3SiO_4Li and H_6SiAlO_7Li clusters, respectively. By comparing the PA value of H_4SiO_4 cluster with that of H_7SiAlO_7 cluster, the latter is smaller than the former by the interaction of Al to O_s. Therefore, the interaction of Al to O_s in silica glass is considered to make the dissociation of H_s from O_s easy, while the dissociation is considered to be prevented from by the affect of Li ion coordinated to nonbridging oxygen.

A plot of PA values against the charges of H_s atoms is shown in Fig. 2. It is interesting to note that the PA values decrease with an increase in the atomic charges of H_s atoms. In other words, the PA values decrease with

Table 2
Calculated bond lengths (Å) and angles (degree) for the model clusters and comparison with experiments

Parameters	Calculation [a]				Observed values
	H_4SiO_4	H_3SiO_4Li	H_7SiAlO_7	H_6SiAlO_7Li	
Si–O	1.657	1.657	1.655	1.661	1.61 [14], 1.62 [15,16], 1.64 [17,18]
Al–O			1.727	1.726	1.72 [14], 1.89 [17], 1.95 [17]
Li–O		1.467		1.475	1.96 [14], 2.00 [16], 2.06 [18]
O–Si–O	109.47	109.47	109.47	109.47	108.8 [18], 109.5 [14], 109.4 [16]
O–Al–O			108.04	108.27	109.7 [14]
Si–O–Al			134.44	135.96	130.0 [17], 134.6 [19], 135.7 [17], 148.1 [14]
Si–O–Li		179.55		179.08	123.3 [14]

[a] Average values of Table 1 are listed.

Table 3
Mulliken atomic charges and proton affinities for $H_{4-x}SiO_4Li_x$ and $H_{7-x}SiAlO_7Li_x$ clusters at the 3–21G+d(Si,Al,O)//STO-3G level

	$H_{4-x}SiO_4Li_x$		$H_{7-x}SiAlO_7Li_x$	
	$x=0$	$x=1$	$x=0$	$x=1$
Atomic charges				
$q(H_s)$	+0.428	+0.408	+0.513	+0.498
$q(O_s)$	−0.802	−0.816	−0.861	−0.865
q(Si)	+1.567	+1.530	+1.654	+1.611
q(Al)			+1.120	+1.123
$q(O_{nb})$		−0.895		−0.885
Proton affinities				
PA [a]	17.69	18.69	15.09	15.95

[a] PA in eV/mol.

increase in ionicity of H_s atoms. Thus, the greater the positive charge on H_s atom, the weaker the H_s–O_s ionic bond and the easier the dissociation of H_s from O_s. The charge of H_s atom is thought to be used as measure of PA.

3.4. Tritium release

Tritium release from lithium silicate and metal doped lithium silicate is thought to be a complicated process which includes bulk diffusion and desorption from the surface. The various chemical forms of tritium are assumed to exit on the surface because of complex surface structures due to irradiation. The tritium was described to have a larger probability for localization in chemical form of [≡Si–O–T] [23]. The chemical nature of tritium in the chemical form of [≡Si–O–T] is understood with the results obtained from the calculations in this study.

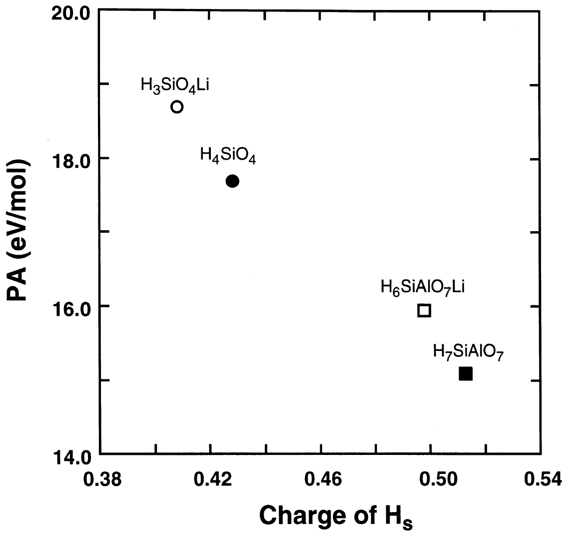

Fig. 2. Proton affinities vs. charges of H_s atoms.

From the ab initio molecular orbital calculations for the model clusters, the dissociation of surface hydrogen is considered to be promoted through the interaction of Al to surface oxygen. The result obtained from the calculations explains the improvement of tritium release from lithium orthosilicate due to doping of Al. Especially, judging from the decrease of dissociation energies due to the interaction, the improvement of tritium release at low temperature is expected for doping of Al. These results obtained from calculations are consistent with the experimental results obtained by Vollath et al. [1].

And also, several tritium release peaks were observed for lithium silicates [23]. Some of them are associated with the chemidesorption of tritiated water from the surface. In this study, the ionicity of surface hydrogen is shown to be weakened by the affect of Li ion which coordinates to nonbridging oxygen in silica glass. This means that the nonlocalized effect of Li ion prevents the tritium release from surface. Several peaks observed for tritium releases are thought to be associated with the degree of nonlocalized effect of Li ions.

4. Conclusions

In this study, we have presented results of ab initio molecular orbital calculations on model clusters $H_{4-x}SiO_4Li_x$ and $H_{7-x}SiAlO_7Li_x$ ($x=0$ and 1). The charge distribution and proton affinity were investigated on the model clusters. By the use of these clusters, the charge and proton affinity of surface hydrogen were shown to be affected by the interaction of Al to surface oxygen and Li ion coordinated to nonbridging oxygen. The following conclusions can be drawn from this study:

(1) The ionicity of surface hydrogen is strengthened by the interaction of Al to surface oxygen. On the other hand, the ionicity is weakened by the nonlocalized effect of Li ion coordinated to nonbridging oxygen.

(2) The proton affinity values decrease with the increase of ionicity of the surface hydrogen.

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