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# Preparation of silicate foams using $HSi(OC_2H_5)_3$ and their $NO_x$ adsorption behavior

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## Abstract

Lithium silicate foams have been prepared by reaction of $HSi(OC_2H_5)_3$ with aqueous lithium silicate solution. During hydrolysis and condensation reactions of ethoxy groups, Si–H bonds were also broken under the base condition of aqueous lithium silicate solution with the evolution of hydrogen gas. The gelation occurred immediately and during the gelation the hydrogen gas produced macro-voids to provide lithium silicate foams. The wall of the macro-voids in the foams was made up of particulate porous gels with about 50 nm-sized particles. The surface of the lithium silicate foams showed the solid-basic property of $H_0 = 9$ and adsorbed the acidic gases of NO and $NO_2$. FT-IR spectrum of both the lithium silicate foams adsorbing NO and $NO_2$ showed an absorption peak at 1385 $cm^{-1}$ assigned to the $\nu_3$ stretching vibration of nitrate species, $NO_3^-$. The absorption peak of $NO_3^-$ disappeared in the samples heated at 500 °C in air.

*Keywords:* Chemical properties; $NO_x$ sorbent; Porosity; Silicate; Sol-gel process

## 1. Introduction

The demands for reduction of nitrogen oxides ($NO_x$) in emission from stationary and mobile sources have been increasing, which promotes not only a search for de$NO_x$ catalysts[1] but also a development for electrochemical de$NO_x$ cells using oxygen-conductive electrolyte.[2] Especially, the electrochemical cell with $NO_x$-selective electrode can reduce $NO_x$ to $N_2$ without any reducing agents even in the presence of $O_2$.[3,4] At low temperatures, however, the reduction of $NO_x$ is difficult for the electrochemical cell because of the low conductivity of oxygen ions in the electrolyte. In order to completely remove $NO_x$ in low-temperature exhaust gas of engine starting, the electrochemical cell needs reversible sorbent of $NO_x$, which can absorb $NO_x$ at low temperatures and release it at cell-working temperatures.

Porous materials prepared by the sol-gel process are attractive for the $NO_x$ sorbent because of controlling pore structure in a wide rage. The sol-gel process, especially using silicon alkoxides as a precursor, provides porous bodies with high surface area such as xerogels and aerogels, as well as meso- and micro-porous bodies derived from organic templates. $HSi(OC_2H_5)_3$ has been known as a precursors for the preparation of silica xerogels with high surface area.[5] These silica xeogels have been generally prepared from $HSi(OC_2H_5)_3$ only under acidic condition because H–Si bonds are unstable under basic conditions. Under basic conditions, however, the generation of hydrogen gas by the break of H–Si bonds is expected to provide macro-pores in silicate gel. In addition, the use of lithium silicate solution as a starting material is also expected for controlling solid acid-base properties of silicate surface, which is a good way for the design of the affinity toward $NO_x$.[6]

In the present paper, lithium silicate foams were prepared by reaction of $HSi(OC_2H_5)_3$ with aqueous lithium silicate solution and the $NO_x$ absorption–desorption behavior of the lithium silicate foams was also investigated.

## 2. Experimental procedure

Hydrido-triethoxysilane $HSi(OC_2H_5)_3$ and aqueous lithium silicate solution (LSS, $Li_2O(SiO_2)_n$, $n = 7.5$) were commercially available from Tokyo Kasei Kogyo Co., Ltd. and Nissan Chemical Industries, LTD., respectively. The solid content of LSS was 20 wt.%. $HSi(OC_2H_5)_3$ was

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added to LSS in the weight ratio of $HSi(OC_2H_5)_3$/LSS = 0.5. The solution was immediately gelled with gas formation to give a lithium silicate foam. The lithium silicate foams were dried at 100 °C and heat-treated at 600 °C. The heat-treated lithium silicate foams were exposed to 500 ppm NO or $NO_2$ diluted by Ar.

FT-IR spectra were recorded on a FT-IR Spectrometer of Herschel FT/IR-610 (JASC Corp.). Samples were ground to a powder, which was measured by the KBr disk-method. The measurement of solid acid-base strengths was carried out with a series of Hammett indicators.[7] $^{29}Si$ NMR spectra were recorded at 59.5 MHz on a Varian spectrometer (UNITY INOVA 300). The spinning rate of samples was approximately 3–4 kHz. The chemical shifts were given with reference to tetramethylsilane (TMS). Microstructure of the lithium silicate foams was observed by a scanning electron microscope (SEM) of JEOL, JSM-6500F. The specific surface area and pore size distribution were evaluated by analyzing the $N_2$ adsorption/desorption isotherms according to the BET method (Autosrb-3B, Quant-Chrome Corp.).

## 3. Results and discussion

Fig. 1 shows the photograph of a typical lithium silicate foam prepared from $HSi(OC_2H_5)_3$ and LSS. During hydrolysis and condensation reactions of ethoxy groups, Si–H bonds were also hydrolyzed under the base condition of aqueous lithium silicate solution with the evolution of hydrogen gas. The gelation occurred immediately and the hydrogen gas during the gelation produced macro-voids to provide the lithium silicate foam. The H–Si bonds in $HSi(OC_2H_5)_3$ were completely decomposed as results from FT-IR and $^{29}Si$ NMR analyses. In the FT-IR spectrum of the lithium silicate foam, the absorption peak of the H–Si bonds at 2195 $cm^{-1}$ disappeared. The $^{29}Si$ NMR spectrum of gel prepared from $HSi(OC_2H_5)_3$ in the acidic condition of HCl gave the peaks of T units corresponding to H–Si(O–)$_3$ as shown in Fig. 2(a). In the lithium silicate foams, however, only the peaks of Q units were observed without the peaks of T units as shown in Fig. 2(b). The peaks of Q units consisted of a large $Q^3$ peak and a shoulder $Q^4$ peak. After heat-treating the lithium silicate foams, the $Q^4$ peak became lager than the $Q^3$ peak. This means that by the heat-treatment, the number of Si-OH bonds was decreased and the silicate network was developed.

Fig. 3 shows the SEM micrograph of the wall of macro-pores in the lithium silicate foams. The wall of macro-pores was made up of particulate porous gels with about 50 nm-sized particles. The foams had the relatively high specific surface area of about 300 $m^2/g$ and the peak of the pore size distribution was 20–30 nm size as shown in Fig. 4. Considering the SEM observation, the pores analyzed by the $N_2$ adsorption/desorption isotherms likely correspond to the voids constructed by packing with the particles in the particulate porous gel structure.

Fig. 5 shows the solid acid-base strengths of the lithium silicate foam, $SiO_2$ gel and $Li_2O$ powder, which were measured with a series of Hammett indicators. The $SiO_2$ gel and $Li_2O$ powder were prepared by hydrolysis

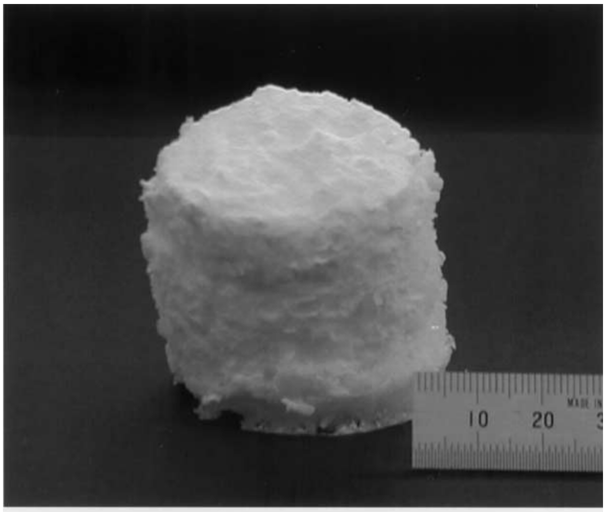

Fig. 1. Lithium silicate foam prepared by reaction of $HSi(OC_2H_5)_3$ with aqueous lithium silicate solution.

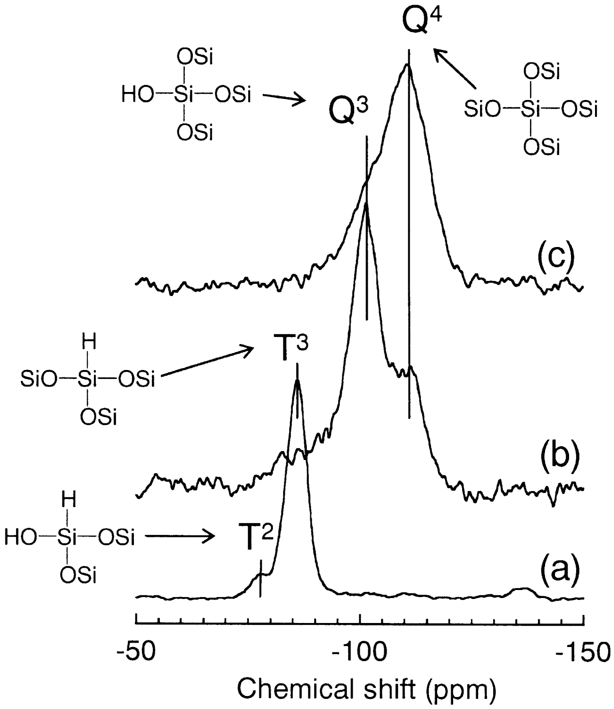

Fig. 2. $^{29}Si$ NMR spectra of (a) gel prepared from $HSi(OC_2H_5)_3$ in the acidic condition of HCl, (b) lithium silicate foam and (c) heat-treated lithium silicate foam.

of Si(OEt)$_4$ and Li(OEt), respectively. The SiO$_2$ gel and Li$_2$O powder were weak acidic and strong basic surfaces, respectively. The lithium silicate foam showed the basic surface of $H_0=9$. This basicity is thought to result from the incorporation of basic lithium into siloxane networks. The basic surface is expected to effectively adsorb the acidic gases of NO$_x$.

The heat-treated lithium silicate foams were exposed to 500 ppm NO or NO$_2$ diluted by Ar and the adsorbed NO and NO$_2$ were analyzed by FT-IR. Comparing the FT-IR spectrum of lithium silicate foam with those of lithium silicate foams exposed to NO or NO$_2$, a sharp absorption peak appeared at 1385 cm$^{-1}$ as shown in Fig. 6. This peak is similar to the peak observed in adsorbed NO on Cu of CuO/Al$_2$O$_3$, which was assigned to the NO$_2$ stretching vibration in NO$_3^-$ in the previous report.[8] In view of simple molecule vibration modes, it is likely that the absorption peak at 1385 cm$^{-1}$ is closer to the $\nu_3$ stretching vibration (see Fig. 6) in four vibration modes of NO$_3^-$ planar regular triangle molecule than the $\nu_1$ stretching vibration in three vibration modes of NO$_2$ isosceles triangle molecule.[9, 10] In lithium nitrate (LiNO$_3$), however, such an absorption peak was not

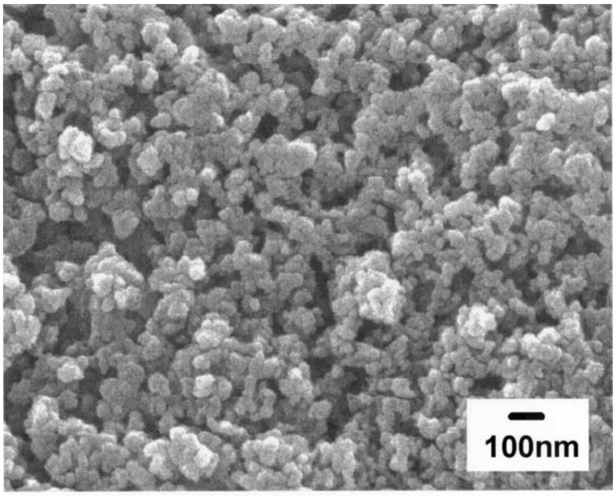

Fig. 3. SEM micrograph of macro-pore wall in lithium silicate foam.

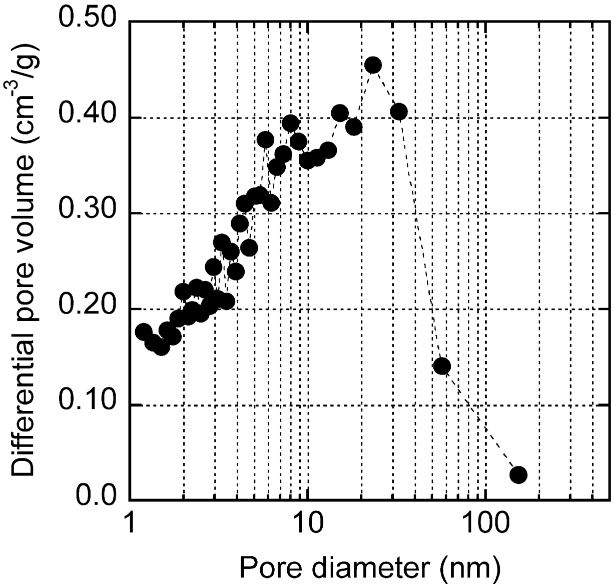

Fig. 4. Pore size distribution of lithium silicate foam.

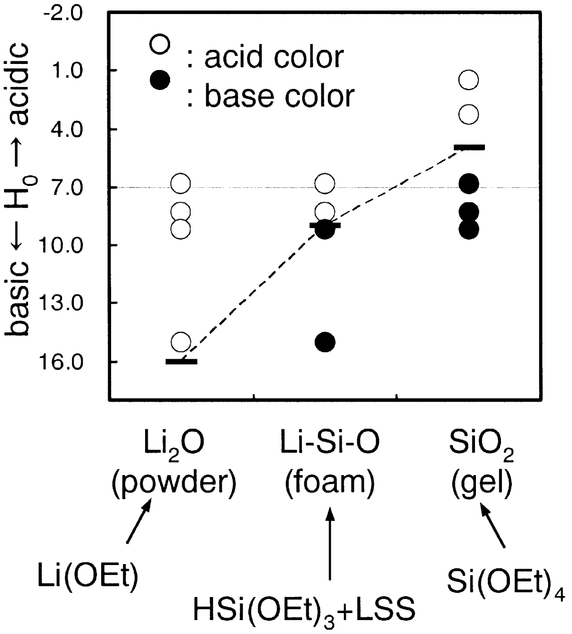

Fig. 5. Solid acid-base strengths of lithium silicate foam, SiO$_2$ gel and Li$_2$O powder measured with a series of Hammett indicators. SiO$_2$ gel and Li$_2$O powder were prepared by hydrolysis of Si(OEt)$_4$ and Li(OEt), respectively.

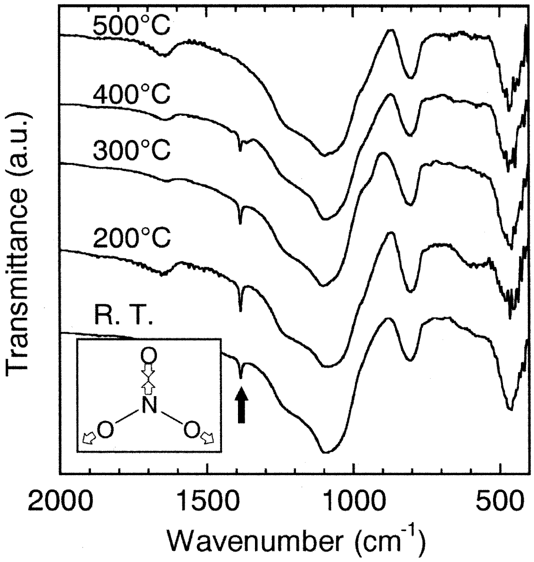

Fig. 6. FT-IR spectra of lithium silicate foam exposed to 500 ppm NO diluted by Ar and NO-adsorbing lithium silicate foam heated at various temperatures in air.

observed at 1385 $cm^{-1}$. Both the adsorbed NO and $NO_2$ are present as nitrate species, $NO_3^-$, but not as lithium nitrate salt on the lithium silicate foams. It can be said that the lithium silicate foams not physically but chemically absorb NO and $NO_2$ gases. Therefore, the oxidation of NO and $NO_2$ to $NO_3^-$ occurred by the absorption. This may be due to surface oxygen atoms and/or adsorbed water of lithium silicate foams. Because the practical exhaust gases from combustions contain oxidizing oxygen gas and water vapor, the lithium silicate foams can effectively adsorb $NO_x$ as nitrate species, $NO_3^-$.

The lithium silicate foams adsorbing NO as $NO_3^-$ were heated at various temperatures in air and measured by FT-IR as shown in Fig. 6. Although the absorption peak at 1385 $cm^{-1}$ was observed up to the heating temperature of 400 °C, it disappeared at the heating temperature of 500 °C, being lower than the decomposition temperature of $LiNO_3$, about 600 °C. Although NO and $NO_2$ gases are chemically adsorbed on the lithium silicate foams, the absorption bonds are likely weaker than bonds of $LiNO_3$ salt. This may be due to the weaker basicity of the surface and/or the structure of lithium-containing siloxane network in the lithium silicate foams.

## 4. Conclusions

The lithium silicate foams were successfully prepared by reaction of $HSi(OC_2H_5)_3$ with aqueous lithium silicate solution. Not only the ethoxy groups of $HSi(OC_2H_5)_3$ were hydrolyzed but also the Si–H bonds were also broken under the base condition of aqueous lithium silicate solution with the evolution of hydrogen gas.

The lithium silicate foams had the wall of the macro-voids consisting of particulate porous gels with about 50 nm-sized particles. The surface of the lithium silicate foams showed the solid-basicity of $H_0 = 9$ and adsorbed the acidic gases of NO and $NO_2$ as nitrate species, $NO_3^-$. The $NO_3^-$ species on the lithium silicate foams were found to be released by heating at 500 °C in air.

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