Spectroscopic Study of Hydrogen-Permeable Membranes Composed of Zeolite Wreckages

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Abstract

Zeolite nanoblock (ZNB), prepared by hydrochloric acid decomposition of Na-A type zeolite, works as a highly efficient hydrogen-permeable membrane. Si and Al K-edge X-ray absorption near edge structure (XANES) spectra were measured for ZNB to clarify the local structures. The Si K-edge XANES spectrum is similar to that of the Na-A type zeolite, but the Al K-edge XANES spectrum is interpreted as a mixture of those of Na-A type zeolite and $AlCl_3 \cdot 6H_2O$. These results suggest that ZNB was mainly composed of a part of the framework of Na-A type zeolite, whose pores are partially filled with small clusters of SiO_2 and $AlCl_3$. As a result of it, the average pore size is much smaller than that of zeolite itself, only permeable to hydrogen molecules.

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1. Introduction

Zeolites are one of silicates in which part of Si atoms are substituted with Al atoms, so-called, ‘aluminosilicates’ and are porous material with a number of holes with fixed sizes, as shown in Fig. 1. These holes are sometimes occupied with water, which is easily desorbed by heating or evacuating. They have more than 150 kinds of crystal structures, depending on the composition of Si and Al, as natural products and synthesized ones. In the zeolite structure, Si is electrically neutral, but Al atoms are negatively charged due to tetrahedral coordination. To maintain the charge neutrality, zeolite crystals take in several kinds of cations in holes close to Al sites. These unique structures enable us to apply to molecular sieves, ion exchangers and catalysts. Among many kinds of zeolites, Na-A type zeolite is the most prototypical with Si : Al composition ratio of 1 : 1, in which both Si and Al atoms are tetrahedrally coordinated with O. These structural units constitutes four-, six- and eight-membered rings (see Fig. 1).

Recently, Nishiyama et al. found that a membrane of Na-A type zeolite wreckages on a porous bycor glass prepared by spin-coating after decomposition of Na-A zeolite with hydrochloric acid works very effectively as a hydrogen filtering film [1, 2]. It is intriguing to investigate why such a film has a function of hydrogen filter and what kind of structural change is induced in the above process.

The X-ray absorption fine structure (XANES) spectroscopy is a powerful method to provide information about local structures around X-ray absorbing atoms and can be applied to any materials which are difficult to study by X-ray diffraction (XRD) methods.

The purpose of this report is to clarify the local structures around Si and Al atoms by measuring XANES spectra at the corresponding K-edges. Electron spectroscopy for chemical analysis (ESCA) spectra were also measured to determine the sample compositions.

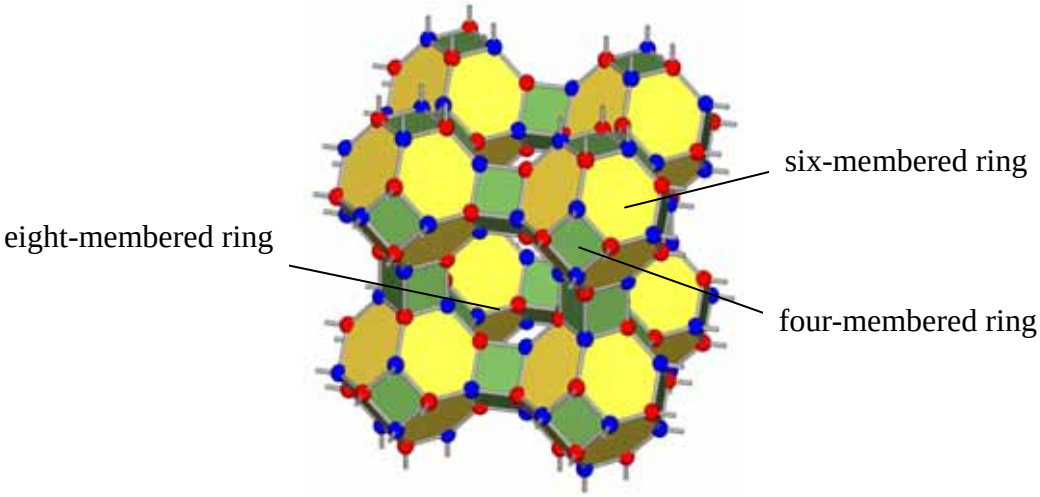

Figure 1. The framework model of Na-A type zeolite. Red balls and blue balls indicate Al atoms and Si atoms respectively. Gray rods are O atoms which connect adjacent an Al atom and a Si atom.

2. Experimental

The sample for XANES measurement was prepared as follows. Na-A type zeolite powders were decomposed by 5 N hydrochloric acid, and then spin-coated on a Si wafer, annealed and dried at 90 °C. We call this sample as ‘zeolite nanoblock (ZNB)’. Powder ZNB samples were used for ESCA and XRD measurements.

Si and Al K-edge XANES measurements were carried out at soft-X-ray double crystal monochromator beamline, BL-10. This beamline is composed of a 10 μm thick Be filter, a Ni coated toroidal mirror, Golovchenko-type double crystal monochromator, I_0 chamber and sample chamber.

InSb(111) and KTP(011) were used as monochromatizing crystals for Si K-edge and Al K-edge XANES measurements, respectively. Sample current was monitored to obtain the total electron yield (TEY) spectra, which were normalized by the drain current from I_0 grid made of Cu.

ESCA spectra were measured with XPS1600 (ULVAC PHI Inc.) in Faculty of Science and Engineering of Ryukoku University, using Al Kα as the X-ray source.

Powder XRD spectrum were also measured to confirm the long range ordering.

3. Results and discussion

Figure 2 shows XRD spectra of the ZNB powder, compared with that of Na-A zeolite powder. This result clearly indicates that ZNB has lost long range ordering.

The Si K-edge XANES spectrum of the ZNB on Si wafer is shown in Fig.3 (2), compared with those of reference materials, Na-A zeolite (1), quartz powder (4) and Si wafer (5).

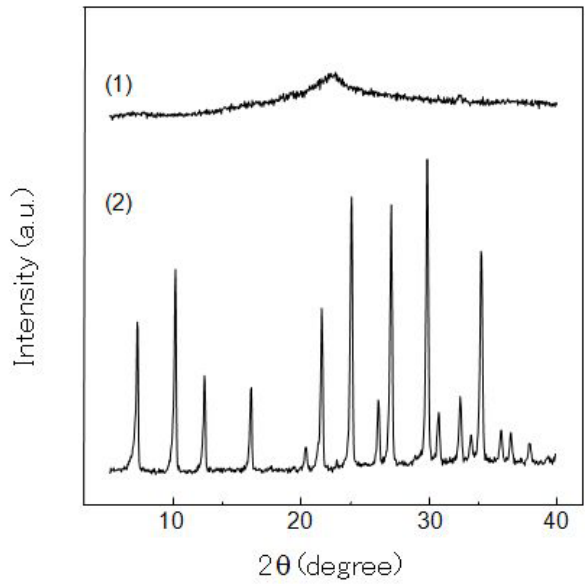

Figure 2. XRD spectrum of (1) the ZNB powder and (2) the Na-A type zeolite powder.

Figure 3 (3) is the extracted spectrum of the ZNB, obtained by subtraction the contribution of the spectrum of Si wafer (5) from the spectrum (2). Close resemblance between the spectra of (1) and (3) suggests that local structure of Si atoms does not change even by acid decomposition, keeping the tetrahedral coordination with O atoms.

Figure 4 (2) shows the Al K-edge XANES spectrum from ZNB, compared with those of reference compounds, Na-A zeolite (1), $AlCl_3 \cdot 6H_2O$ powder (3), and α-Al_2O_3 powder (4). As described above, the local structure around the Al atom in zeolite is similar to that of Si, since part of Si atoms are simply substituted by Al atoms. Thus, the spectral profile of Al K-edge XANES of zeolite is similar to that of Si- K-edge XANES. However, the spectrum of the ZNB is significantly different from that of Na-A type zeolite. At first, we thought intuitively that Al atoms are melted out from the framework of zeolite by acid decomposition and form aluminum oxides such as α-Alumina, but it turned out to be not correct (see Figs.4 (2) and (4). It is much closer to that of $AlCl_3 \cdot 6H_2O$ (3), but more careful inspection of the spectrum (1), for example the white line at 1857.5 eV and broad shoulder peaked at 1585 eV, indicates some contribution of Na-A type zeolite.

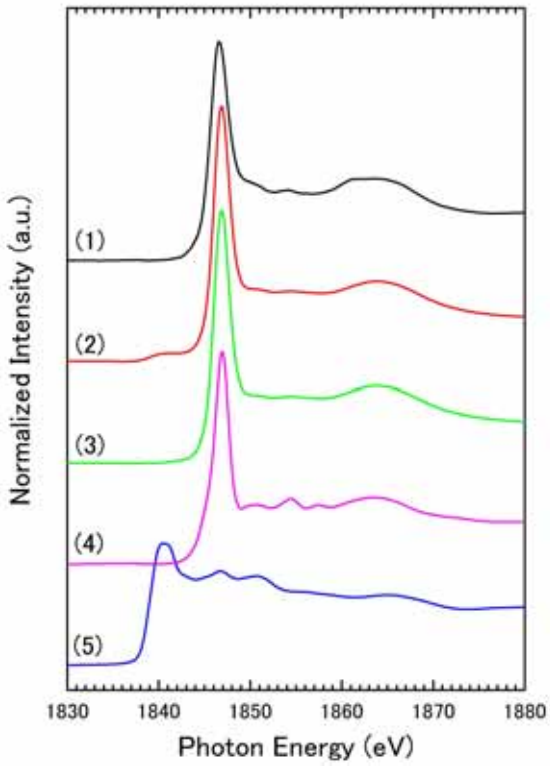

Figure 3. Si K-edge XANES spectra.
(1) Na-A type zeolite powder, (2) ZNB on Si wafer, (3) the subtraction spectrum (5) from (2), (4) Quartz powder, (5) Si wafer

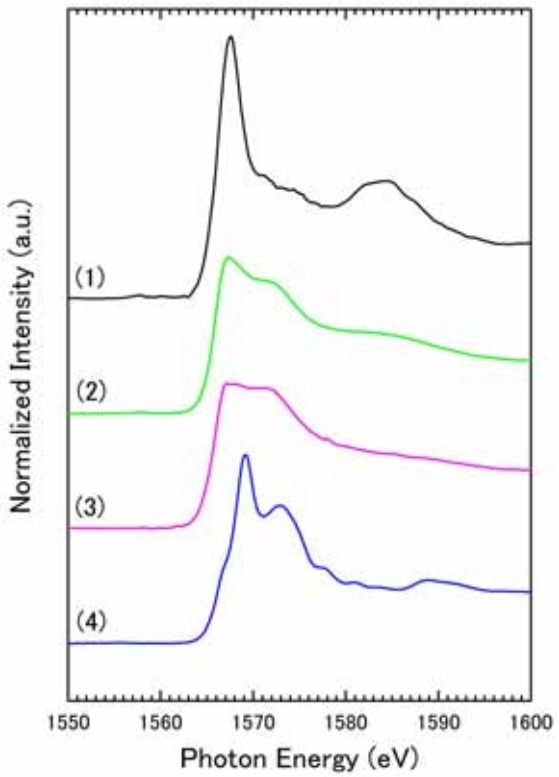

Figure 4. Al K-edge XANES spectra. (1) Na-A type zeolite powder, (2) ZNB on Si wafer, (3) $AlCl_3 \cdot 6H_2O$ powder, (4) α-Al_2O_3 powder

To analyze the spectrum from ZNB quantitatively, it was simulated by the composite spectra from $AlCl_3$ and Na-A zeolite with different component ratios. As shown in Fig. 5, the spectrum of the ZNB was well reproduced by the summed spectrum of 86 % from $AlCl_3$ and 14% from zeolite. This result suggests that 86 % of Al atoms are octahedrally coordinated with Cl and remained 14 % of Al atoms are tetrahedrally coordinated with O.

To confirm the formation of $AlCl_3$ in the ZNB, ESCA spectra were obtained for the ZNB powder and that after washing with water, as well as Na-A type zeolite, as shown in Fig. 6. The intensity ratio of Si : Al : Na of the ZNB powder is quite similar to that of Na-A zeolite. However, a significant peak was found at 200 eV, which is assigned to Cl 2*p*. The spectrum (3) shows that Cl peak disappears, as well as Al and Na peaks by washing with water. These results show that some chlorides were formed by addition of hydrochloric acid to Na-A type zeolite and was washed out by water treatment. Simultaneous decrease of Al and Na by washing suggests that chloride compound is $AlCl_3$ and/or NaCl, which is consistent with XANES results.

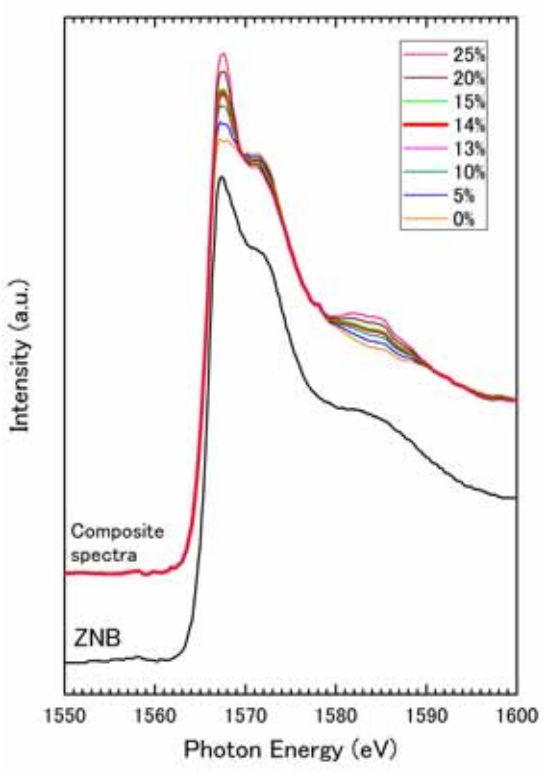

Figure 5. Composite spectra of Na-A type zeolite and $AlCl_3 \cdot 6H_2O$. Index of upper right in graph shows component ratios of the spectrum of Na-A type zeolite.

Combining the results of XRD, XANES and ESCA, we can deduce the following process. Na-A zeolite is decomposed by addition of hydrochloric acid. In the obtained product, Si atoms kept their four coordinated structure with O, but most of Al atoms in the zeolite framework were melted out and formed $AlCl_3$. As a result, zeolite structure has been collapsed and the s in the aluminosilicates are broken and most of six- and four-membered rings are also broken. Only a few small membered rings are remained, but these rings are blocked by SiO_2, $AlCl_3$ and other residues. Although it is difficult to explain definitely, ZNB is composed of stacked wreckages of Na-A zeolite framework whose holes are blocked by SiO_2, $AlCl_3$ and other residues. Zeolite has large holes, but the blocked holes of the ZNB are sufficiently small for only hydrogen molecules to be permeable.

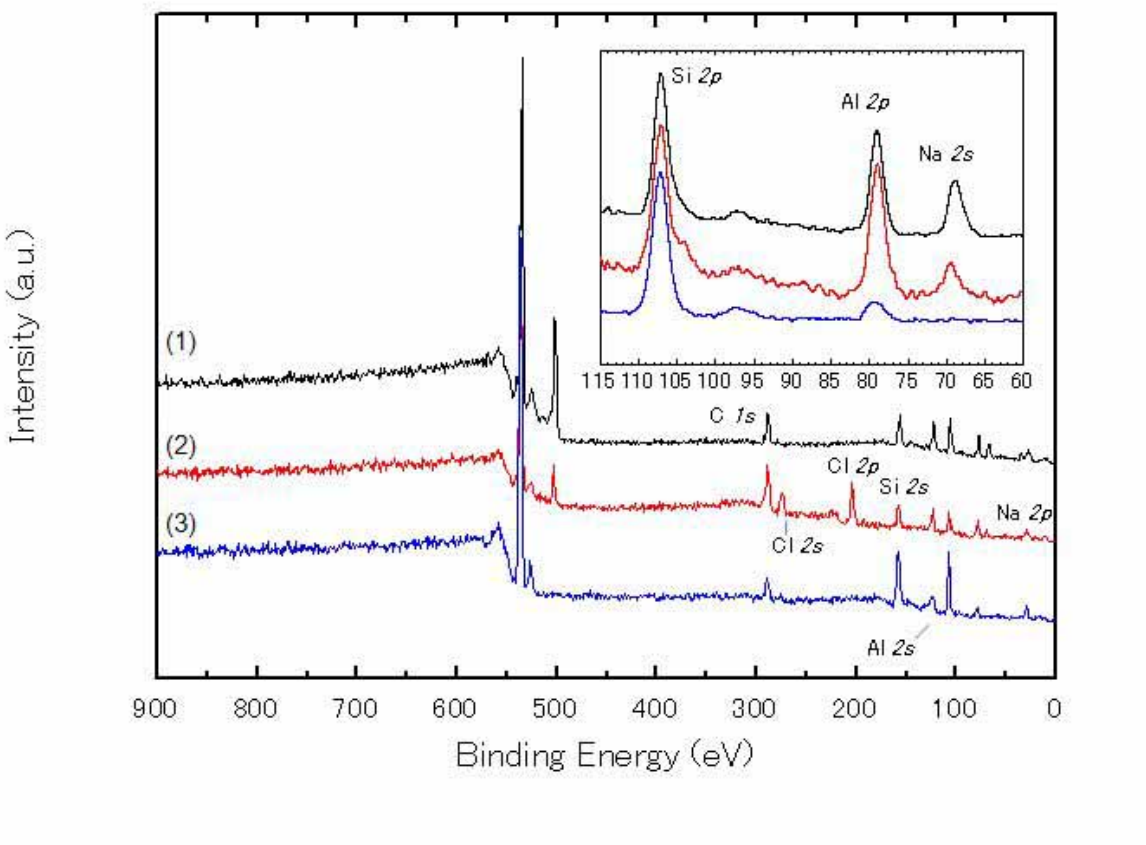

Figure 6. ESCA spectra of the ZNB powder and the comparison samples.
(1) Na-A zeolite powder, (2) ZNB powder, (3) ZNB powder which washed

Acknowledgement

We acknowledge Prof. Fujiwara of Ryukoku University, who generously allowed us to use the ESCA equipment in his laboratory.

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