Synthesis of Sodalite in Nonaqueous Solvents

Ryozi HINO, Kenji TORIGOE and Yoshiro MORIYA

Department of Chemistry, Faculty of Science, Shimane University, 1060, Nishikawatsu-cho, Matsue-shi, Shimane 690

In an attempt to prepare zeolites of a new type or those having new surface properties, their synthesis in a nonaqueous solvent system using methanol, 2-propanol, ethylene glycol or monoethanolamine was studied. Sodalite of high crystallinity was obtained using monoethanolamine as solvent, and tetraethoxysilane, aluminum triisopropoxide, and sodium hydroxide as raw materials. The synthesis conditions were $\text{SiO}_2/\text{Al}_2\text{O}_3=2$, $\text{Na}_2\text{O}/\text{SiO}_2=5$, solvent/$\text{Na}_2\text{O}=90$ molar ratio at 150°C, and 22-490h of aging time. The properties of these crystals were compared with those obtained from 2-propanol containing water (1.2 vol% of solvent) and from pure water. Our crystals had a slightly larger lattice constant and adsorbed a large amount of N2 gas; in particular, the shape of the adsorption isotherm was unique compared with those of others. This greater adsorption may be attributed to adsorption at the inner surface, that is, the windows of sodalite allow the penetration of N2 into the pore structure. This was also suggested by the larger lattice constant.

Key-words : Sodalite, Nonaqueous solvent, Synthesis, Monoethanolamine, Adsorption, Surface property

1. Introduction

Much interest on the characteristics of the zeolite surface, adsorption, molecular sieving, ion exchange and catalysis, has been raised in the field of science and technology, and various kinds of crystals have been synthesized.

In general, zeolites are hydrothermally synthesized from silica, alumina, and alkali sources and water at temperatures above 100°C and correspondingly elevated pressures.1) The initial attempt at synthesis of zeolites by Bibby and Dale2) using an organic solvent instead of water drew much attention to synthesis in a nonaqueous solvent. Their success in obtaining sodalite from such a reaction system led to further investigations on the synthesis of zeolites in nonaqueous systems.3)-9)

We have focused our attention on the effect of ethanol derived from hydrolysis of tetraethoxysilane on the products, because we synthesized zeolites using a metal alkoxide different from conventional starting materials.10,11) We attempted the synthesis of a new type of zeolite or zeolite with a known chemical structure but new surface properties in a nonaqueous system using mainly methanol, 2-propanol, ethylene glycol and monoethanolamine as solvent.

In this paper, the results of syntheses using various solvents, in particular, the comparison of the crystals obtained from the perfect nonaqueous system of monoethanolamine, from 2-propanol containing a small amount of water and from pure water, will be described. These crystals were characterized by XRD, chemical analysis, DTA–TG, IR spectroscopy and gas adsorption methods.

2. Experiments

2.1 Reagents

The starting materials for synthesis were as follows. The sources of alumina were aluminum triisopropoxide (min 95.0%) and sodium aluminate (min 88.0%). The sources of silica were tetraethoxysilane (min 99.9%) and anhydrous sodium silicate (min 91.0%) and fumed silica (Aerosil 200), (min 99.9%). The source of alkali was sodium hydroxide (min 96.0%). The additives were tetramethylammonium bromide (min 99.0%) and ammonium chloride (min 99.0%). The organic solvents used were methanol (min 99.6%), 2-propanol (min 99.5%), ethylene glycol (min 99.5%) and monoethanolamine (min 99.0%). These solvents were distilled carefully using LMS4A as desiccant.

2.2 Synthesis

The compositions of starting materials were $\text{SiO}_2/\text{Al}_2\text{O}_3=-100$ (∞ means aluminium-free), $\text{Na}_2\text{O}/\text{SiO}_2=0.12-6.0$, solvent/$\text{Na}_2\text{O}=26.7-1000$, and $\text{TMA}_2\text{O}/\text{SiO}_2=0.1$. In methanol, 2-propanol and ethylene glycol systems, the synthesis proceeded as follows. A fixed quantity of sodium hydroxide was added to a glass flask (500 ml) containing an organic solvent and the flask was shaken well. The sources of alumina were placed in another flask and mixed thoroughly with the solvent. Then the sources of silica were added to this flask. Finally the contents of the former flask were transferred to the latter one and shaken well. An additive was then supplemented, if necessary. To prevent evaporation of the solvent and adsorption of water vapor, the flask was equipped with a glass tube that was connected to a
The synthesis of the reference sample of sodalite was carried out in pure water as follows. The compositions of starting materials were SiO$_2$/Al$_2$O$_3$=2, Na$_2$O/SiO$_2$=8 and H$_2$O/Na$_2$O=34.7. After fixed amounts of sodium aluminate and sodium silicate were placed in a flask, sodium hydroxide solution was added, and the reactants were thoroughly dissolved by mechanical stirring at 30°C for 24h. Then the flasks were kept for a fixed time at 65°C for methanol, 80°C for 2-propanol, 150°C for ethylene glycol and monoethanolamine and 100°C for water. After aging for a fixed time, the solid phase was filtered off and washed with water until the pH of the washing was equal to 8.0, and then dried at 110°C for 24h.

2.3 Product characterization

The degree of crystallinity was measured by XRD (Toshiba ADG301 Cu Kα, 30kV, 20mA, Ni filter, G.M. detector) using TiO$_2$ as the internal standard. Chemical analysis was carried out using a Hitachi atomic absorption analyzer Model 208 for aluminum and sodium, and gravimetric analysis for silicon. Thermal properties were investigated by DTA–TG (Shimadzu DTG–40). IR spectra were measured by the KBr wafer technique using the Hitachi infrared spectrometer Model 260–50. The adsorption of N$_2$ gas was measured volumetrically at the boiling point of liquid nitrogen. The samples were heated at 300°C for 2h under atmospheric pressure and degassed under vacuum of 1.333 × 10$^{-3}$ Pa for 30 min prior to adsorption.

In order to clarify the surface properties of the crystals, the adsorptions of water, methanol, benzene, cyclohexane and pyridine vapors were measured under 7998 Pa, that is, saturated vapor pressure, at 41.5°C for water, 11.4°C for methanol, 15.4°C for benzene, 14.7°C for cyclohexane and 46°C for pyridine. The adsorption equilibrium was presumed to be attained after 96h.

3. Results and discussion

3.1 Crystalization of sodalite

The results of synthesis using tetraethoxysilane, fumed silica, aluminum trisopropoxide, sodium hydroxide and methanol as solvents with different SiO$_2$/Al$_2$O$_3$, Na$_2$O/SiO$_2$ and solvent/Na$_2$O molar ratios are shown in Table 1. In spite of long aging times, most of the runs did not produce a solid phase. Only an amorphous phase and an unknown phase were obtained using fumed silica as the silica source and ammonium chloride as additive, respectively. In the monoethanolamine system, the sources of alumina were placed in a flask and mixed thoroughly with the solvent. The sources of silica were added to the flask which was then shaken well. Then sodium hydroxide and residual solvent were added. Other conditions were the same as above.

Table 1, the conditions of SiO$_2$/Al$_2$O$_3$=∞, Na$_2$O/SiO$_2$=0.75, and solvent/Na$_2$O=53.4 corresponds to modifications of Bibby and Dale's condition for the formation of silica sodalite.

Table 2 and Fig. 1 described in Section 3.2 show the results for the 2-propanol system. The crystals were obtained at SiO$_2$/Al$_2$O$_3$=2, Na$_2$O/SiO$_2$=5, solvent/Na$_2$O=90 and 120h of aging time. Crystal growth did not proceed beyond this aging time under these conditions. We called this phase a "precursor" of sodalite (D). Precursor D did not change in spite of the addition of water (0.6 mol%) in solvent. However, precursor D became an intermediate (C) upon addition of more water (0.8 mol%). We called this solid phase an "intermediate" having low crystallinity. With further addition of 0.9 vol% water, the sodalite (B) was obtained, and with the addition of 1.2 vol% water, a crystal (A) of high crystallinity was obtained. On the other hand, solid phase B was also obtained when tetramethylammonium bromide was added, and an unknown phase was formed when ammonium chloride was added to the reactant. Using the same molar ratio as that of Bibby and Dale in the presence of fumed silica, the product was only the amorphous phase. In this 2-propanol system,

<table>
<thead>
<tr>
<th>SiO$_2$/Al$_2$O$_3$, Na$_2$O/SiO$_2$, Solvent/Na$_2$O</th>
<th>Aging/h</th>
<th>Product</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>infinite, 0.75, 53.4</td>
<td>120</td>
<td>Amorphous</td>
<td>d</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>90</td>
<td>120</td>
</tr>
<tr>
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<td>0.5</td>
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<td>10</td>
<td>0.5</td>
<td>90</td>
<td>2972</td>
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<td>0.5</td>
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<tr>
<td>40</td>
<td>0.5</td>
<td>90</td>
<td>1669</td>
</tr>
<tr>
<td>50</td>
<td>0.5</td>
<td>90</td>
<td>1669</td>
</tr>
</tbody>
</table>

1) Aging time (h) at 65°C, 2) a: Si[OC$_2$H$_5$]$_4$, Al[OC$_2$H$_5$]$_3$, d: Fumed silica, e: NH$_4$Cl/SiO$_2$=0.1, 3) Al-free, 4) Unknown phase, 5) No precipitation

<table>
<thead>
<tr>
<th>SiO$_2$/Al$_2$O$_3$, Na$_2$O/SiO$_2$, Solvent/Na$_2$O</th>
<th>Aging/h</th>
<th>Product</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>5</td>
<td>90</td>
<td>120</td>
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<td>5</td>
<td>90</td>
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</tr>
<tr>
<td>2</td>
<td>5</td>
<td>90</td>
<td>120</td>
</tr>
<tr>
<td>infinite</td>
<td>72h</td>
<td>Amorphous</td>
<td>d</td>
</tr>
</tbody>
</table>

1) Aging time (h) at 80°C, 2) a: Si[OC$_2$H$_5$]$_4$, Al[OC$_2$H$_5$]$_3$, d: Fumed silica, e: NH$_4$Cl/SiO$_2$=0.1, f: H$_2$O/solv.=0%, g: H$_2$O/solv.=0.8%, h: H$_2$O/solv.=0.8%, i: H$_2$O/solv.=1.0%, j: 2,2,2-Trifluoroethanol/SiO$_2$=0.8, 3) a: Highly crystalline sodalite, B: Sodalite, C: Intermediate, D: Precursor, 4) Unknown phase, 5) Al-free
over 0.9 vol% of water was necessary to obtain sodalite of high crystallinity.

Table 3 shows the results for the ethylene glycol system. In this system, anhydrous sodium silicate and sodium aluminate were used in addition to tetraethoxysilane and aluminum triisopropoxide. As shown in Table 3, most of the runs did not produce a solid phase, or the products were almost amorphous even if solid phases were obtained. However, using the same molar ratio as that of Bibby and Dale, well-developed crystals of unique silica sodalite were obtained.

Table 3 shows the results for the ethylene glycol system. In the perfect nonaqueous solvent, SiO2/Al2O3=2, Na2O/SiO2=5, and solvent/Na2O =90, at 150°C with 22-490h of aging time, we obtained well-developed crystals of sodalite for the first time. However, using the same molar ratio as that of Bibby and Dale, crystals were not obtained.

3.2 XRD of sodalite

Figure 1 shows the XRD patterns of sodalite obtained from the nonaqueous 2-propanol and the 2-propanol solvent containing a small amount of water (0.6-1.2 vol% in solvent). As mentioned above, the effect of water content in the solvent on the crystallinity was marked. The small difference of the addition of 0.1 vol% of water significantly affected the growth rate from the lower-order to the higher-order structure.

The XRD patterns of sodalite crystals obtained from 2-propanol containing water (1.2 vol%), monoethanolamine and pure water are shown in Fig. 2. The crystallinity of sodalite obtained from pure water was slightly higher than that of the others, but that of sodalite obtained from monoethanolamine and 2-propanol containing water (1.2 vol%) was almost the same.

As shown in Fig. 2 the crystals revealed lower diffraction angles (2θ) in the order of monoethanolamine, 2-propanol containing water (1.2 vol%), and pure water. The shift of the angles denotes the differences in the lattice constants. The lattice constants of sodalite were 0.899 nm (monoethanolamine), 0.893 nm (2-propanol containing water), 0.889 nm (pure water) and 0.877 nm (ethylene glycol).

3.3 Chemical composition of sodalite

The results of chemical analysis are shown in Table 5. The crystals obtained from 2-propanol contain...
taining water (1.2 vol%) revealed the decrease of Na and the increase of Si content with increasing degree of crystallinity. This indicates that crystals showing a lower degree of crystallinity contain lower-order materials, i.e., they contain residual Na ions that were not washed out thoroughly. The crystals of higher crystallinity had nearly the same chemical compositions in all of the solvent systems studied here.

3.4 DTA–TG of sodalite

DTA–TG measurements were carried out and the results obtained from crystals of higher crystallinity are shown in Fig. 3. The thermal behavior of the crystals obtained from 2-propanol containing water (1.2 vol%) revealed endothermic peaks (100–200°C), an exothermic peak and changes of TG (around 600°C), and an exothermic peak (around 900°C). These thermal behaviors were observed in all samples. A marked decrease of weight was observed in the samples of lower crystallinity compared with those of higher crystallinity. As mentioned above, this is because the crystals of lower crystallinity contained the lower-order material, so that the quantity of solvent molecules in the lower-order material was greater than those in the crystals of higher crystallinity.

The XRD results obtained after heat treatment at various temperatures revealed that the endothermic peak at around 200°C was due to dehydration or loss of solvent, and that the crystals changed slightly at 550°C, with nepheline being formed at 900°C. The samples exhibited a greyish color at 500–700°C. These suggest that in the range of 600–700°C, 2-propanol molecules included in the crystals were oxidized and decomposed by heating.

The crystals obtained from monoethanolamine showed a large exothermic peak accompanied by the decrease of weight at around 550°C. Since XRD showed that the crystal structure was maintained at approximately 600°C, the exothermic peak was due to the oxidation of solvent bound on the outer surface. The decrease of weight observed at around 900°C indicated the loss of solvent molecules from the internal structure of crystals.

The crystals obtained from pure water revealed some endothermic peaks owing to dehydration at different temperatures below 300°C, which suggested various states of water molecules in the crystal structure. That is, water molecules may exist in the \( \beta \)-cage as free molecules, hydrated water ions, molecules linked to the lattice oxygen and the surface-hydroxyl groups by hydrogen bonds, and as the

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**Table 5. Chemical Compositions of Sodalite**

<table>
<thead>
<tr>
<th>Sample</th>
<th>X’’</th>
<th>Y’’</th>
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</thead>
<tbody>
<tr>
<td>I</td>
<td>1.1</td>
<td>2.4</td>
</tr>
<tr>
<td>II</td>
<td>1.6</td>
<td>2.2</td>
</tr>
<tr>
<td>III</td>
<td>1.8</td>
<td>2.1</td>
</tr>
</tbody>
</table>

1) 1: 2-propanol containing 1.2 vol% water  
   II: monoethanolamine system  
   III: pure water system  
   A: Highly crystalline sodalite, B: Sodalite  
   C: Intermediate, D: Precursor

2) X’’Na₂O·Al₂O₃·Y’’SiO₂;
hydroxyl group itself.\textsuperscript{12)}

3.5 IR spectra

IR spectra of sodalite of high crystallinity are shown in Fig. 4, in which 1096 cm\(^{-1}\) (very weak shoulder) and 986 cm\(^{-1}\) (strong) were assigned to the asymmetric stretching mode \(\langle\text{OT} \rightleftharpoons \text{O}\) (T: Al or Si);\textsuperscript{13} 729 cm\(^{-1}\) (medium), 701 cm\(^{-1}\) (medium weak) and 660 cm\(^{-1}\) (medium) were assigned to the symmetric stretching mode \(\leftrightarrow\text{OT} \rightleftharpoons \text{O}\);\textsuperscript{13} and 461 cm\(^{-1}\) (medium strong) and 432 cm\(^{-1}\) (medium strong) were assigned to the T-O bending mode.\textsuperscript{13)} IR spectra showed that sodalite crystals grew well and exhibited nominal difference from each other in the structure.

3.6 Adsorption of N\(_2\) gas

The adsorption isotherms of sodalite crystals obtained from various solvents are shown in Fig. 5. The crystals obtained from 2-propanol containing 1.2 vol\% water and from pure water revealed almost the same values and nearly the same shapes of isotherms. Judging from the crystal structure, that is, the diameter of the 6-oxygen rings\textsuperscript{14)} being smaller than that of the N\(_2\) molecule,\textsuperscript{15)} this amount of adsorption is that at the outer surface of the crystals. However, the crystals obtained from monoethanolamine revealed a large amount of adsorption and a unique shape of the adsorption isotherm compared with other sodalites. This adsorption isotherm was fitted well by the Langmuir equation. This adsorption may be attributed to not only the outer surface but also the inner surface; that is, the window of this sodalite may enable N\(_2\) gas to penetrate into the pore structure. This was inferred from the larger lattice constant of sodalite in monoethanolamine compared with others. However, the mechanism of adsorption of N\(_2\) gas on this sodalite must be studied in detail hereafter.

Specific surface areas were evaluated by fitting the Langmuir equation to N\(_2\) adsorption. The sodalites obtained from 2-propanol containing various amounts of water had almost the same surface areas (26–29 m\(^2\)/g). The sodalite obtained from pure water had a slightly larger surface area (36 m\(^2\)/g) compared with that from 2-propanol containing water (1.2 vol\%). The sodalite from the monoethanolamine system had the largest surface area (80 m\(^2\)/g).

3.7 Adsorption of various vapors

The amounts of water, methanol, benzene, cyclohexane and pyridine vapors adsorbed on the crystals obtained from the monoethanolamine system are shown in Table 6. The order of adsorption was water > methanol > benzene ≅ cyclohexane ≅ pyridine;

![Fig. 4. IR spectra of sodalite crystals obtained from 2-propanol containing 1.2% water (1), monoethanolamine (2) and pure water (3).](image)

![Fig. 5. Adsorption isotherms of N\(_2\) gas on sodalite crystals obtained from 2-propanol containing 1.2% water (1), monoethanolamine (2) and pure water (3).](image)

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Amount of adsorption (^{\text{\textsuperscript{1}}\text{ at saturated vapor pressure}}) (mmol g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>49.6</td>
</tr>
<tr>
<td>methanol</td>
<td>15.4</td>
</tr>
<tr>
<td>benzene</td>
<td>7.13</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>6.92</td>
</tr>
<tr>
<td>pyridine</td>
<td>6.37</td>
</tr>
</tbody>
</table>

\(^{1}\text{ at saturated vapor pressure}\)
however, since there was nearly no difference in adsorption among benzene, cyclohexane and pyridine, which have almost the same molecular size but different chemical characteristics, the crystals are assumed not to be polar, but rather, somewhat hydrophobic.

4. Conclusions

Syntheses were carried out in various nonaqueous solvents. In the 2-propanol system, the precursor persisted up to the addition of 0.6 vol% water, and became sodalite of low crystallinity upon the addition of 0.8 vol% water. With the addition of 0.9 vol% water, it grew further into sodalite crystals, and with addition of 1.2 vol% water, sodalite of the highest crystallinity was obtained. The solid phase rapidly changed to the crystal phase of higher crystallinity with addition of about 0.8 vol% water. The small amount of water was found to considerably affect crystallization.

In the monoethanolamine system, that is, a perfect nonaqueous system, sodalite of higher crystallinity was obtained under the conditions of SiO$_2$/Al$_2$O$_3$=2, Na$_2$O/SiO$_2$=5, solvent/Na$_2$O=90, at 150°C with 22-490 h of aging.

The characteristics of the crystals obtained from the three different solvents were compared. Crystals obtained from monoethanolamine revealed the largest lattice constant, according to XRD measurement. These crystals also adsorbed greater amounts of N$_2$ gas and had a unique adsorption isotherm. There was no marked difference among sodalites obtained from the three different systems with respect to IR spectra and chemical compositions.

References