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Silica Sodalite without Occluded Organic Matters by Topotactic Conversion of Lamellar Precursor

Takahiko Moteki, Watcharop Chaikittisilp, Atsushi Shimojima, and Tatsuya Okubo*

Department of Chemical System Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan

Received September 2, 2008; E-mail: okubo@chemsys.t.u-tokyo.ac.jp

A bottom-up approach has attracted materials chemists and has been a focus of strategy to innovate a priori materials with desired structures and properties.[1] Strategic building blocks can be designed to structure-direct the formation of objective materials, leading to a wide spectrum of desired functions. Such a concept has been applied to synthesize zeolites thus far; however, no attempts have succeeded partly due to a plethora of hydrothermal reactions in zeolite syntheses.[2] Moreover, zeolites are formed as metastable phases, and their syntheses are kinetically controlled; hence, the crystallized products are hardly predicted.[2b] Recently, several novel zeolites have been obtained from layered silicates by topotactic dehydration-condensation, namely, MWW, FER, CDS-1, Nu-6(2), EU-20b, RUB-24, and RUB-41.[3] During conversion, condensation between two silanol groups on the surfaces of neighboring layers occurs spontaneously upon the thermal treatment without layer breaking or additional silicate species; thereby zeolites with structures identical to their mother layers are obtained. This method thus enables us to predict the resulting products.

Sodalite, one of the most traditional zeolites, is constructed by connecting sodalite cages ($4^6 6^8$ cages) through their single 4- and 6-rings; therefore, small windows of ca. 2.2 Å free diameter allow only small molecules, i.e., He, NH_3, H_2O, and H_2, and some ions to pass through.[4] The micropores of sodalite, however, have not been used effectively because guest species are trapped in the cages during synthesis. In aluminosilicate sodalite, cations compensating for framework charges, together with water or anions, are occluded in the cages. In pure-silica analogues, on the other hand, organic matter used as a solvent and/or structure-directing agent (SDA) is trapped in the cages, and thereby pores are inaccessible.[5] Upon guest removal, the framework structure has been collapsed.

Here, we report novel silica sodalite without occluded organic matter synthesized by topotactic conversion of layered silicate precursor; hence, its micropores can be utilized more effectively. Organic-free pure-silica zeolite has been expected to be used as low-k materials for computer chips and fillers in composite membranes.[6] Organic-free pure-silica sodalite would outperform MEL and MFI zeolites in low-k applications due to its lower framework density. Moreover, sodalite would be a promising material for membrane-based H_2 separation. Our attempts were started by considering several small parts with layered structures that can build the sodalite framework. We found that each single sheet of the (110) plane of sodalite is identical to RUB-15 layered silicate, in which tetramethylammonium (TMA) cations compensating for the negative charges ($Si-O^-$) of the silicate layers and water are occluded.[7] Hence, silica sodalite should be obtained by topotactic conversion of RUB-15; however, all attempts to condense the silanol groups on the layers by calcination to form sodalite have been unsuccessful.[7] In this report, we have developed a new route to shorten synthesis time of RUB-15 (1 week vs 1 month) by starting from the hydrated crystals of double four-ring $8TMA(Si_8O_{20}) \cdot xH_2O$. We expected that the pre-existence of plenty
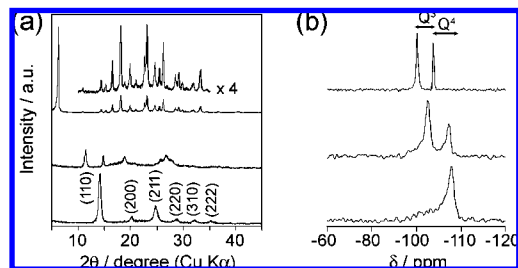

Figure 1. XRD patterns (a) and ^{29}Si MAS NMR spectra (b) of RUB-15 (top), acetic acid-treated RUB-15 (middle), and sodalite (bottom), where XRD peaks are indexed with the crystallographic planes of sodalite.

of 4-rings in the starting precursor would favor the formation of RUB-15, the 4-ring-rich framework, in a shorter time. RUB-15 was obtained by pseudo-solid-state transformation of the hydrated crystals by heating them without additional water in a closed autoclave.[8]

The $Si-O^-$ sites on the layers should be converted to the more adequate $Si-OH$ groups to enhance the condensation between neighboring layers; therefore, acid treatment is necessary. RUB-15 was treated with HCl(aq) with varying pH and time, and then the HCl-treated RUB-15 was calcined to condense the silanol groups; however, the obtained products were amorphous.[8] Following successes in the synthesis of zeolite RUB-24,[3f,9] intercalation of organic species into the layered silicates has been considered as an essential step. Moreover, the neighboring layers of RUB-15 have to be shifted half the unit cell along the c axis to achieve pure silica sodalite.[8] In the case of RUB-24, small carboxylic acids used as the intercalating agent decreased the interlayer distance without shifting the layers.[9] In the case of RUB-15, however, we expected that the use of small carboxylic acids would shorten the distance between the layers upon guest exchange and simultaneously translate individual layers along directions parallel to the layers (bc plane) because the acids could be fit over the sodalite haft-cups and hence somewhat interact with the layers.

After treatment with acetic acid (AcOH), the interlayer distance was decreased from 14.0 to 7.7 Å (Figure 1a). The poor quality of the XRD pattern of the AcOH-treated sample is presumably due to the different environments of the acids between the layers. The ^{13}C CP/MAS NMR spectrum displays two resonances around 20 ppm originated from methyl groups and three resonances around 170−180 ppm attributed to carboxyl groups.[8] We speculate that there are at least three different environments, i.e., AcOH adsorbed on the external surface, AcOH occluded in the interlayer, and esterified products of AcOH and silanol groups. No resonances arising from TMA^+, around 56 ppm, were observed, confirming that $Si-O^-TMA^+$ groups disappeared upon the acid treatment.

As shown in Figure 1a (bottom), silica sodalite was obtained by heating the AcOH-treated samples at 800 °C. To the best of our knowledge, this is the third zeolite, following MWW and FER,
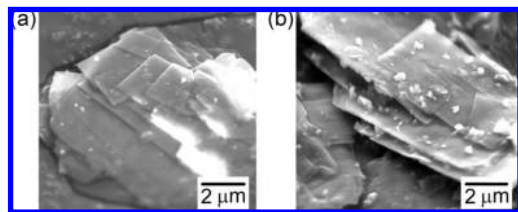
Figure 2. FE-SEM images of (a) RUB-15 and (b) obtained sodalite.

that can be synthesized both by direct hydrothermal reaction and by topotactic conversion. The condensation of silanol groups was confirmed by ^{29}Si MAS NMR shown in Figure 1b. RUB-15 and the AcOH-treated product display two signals assigned to Q^3 ((SiO)$_3$*Si*OH or (SiO)$_3$*Si*O$^-$) and Q^4 ((SiO)$_4$*Si*) sites with the same Q^3/Q^4 ratio of 2. The resonances of RUB-15 at $\delta = -100.4$ (Q^3) and -107.6 (Q^4) are shifted to $\delta = -105.1$ and -114.5, respectively, after AcOH treatment, probably due to the change in the averaged Si$-$O$-$Si bond angles in addition to the conversion of Si$-$O$^-$ to Si$-$OH.[10] The Q^3/Q^4 ratio drastically decreases after calcination, indicating that the Q^3 silicon sites condensed into the Q^4 ones. However, the presence of Q^3 silicon reveals that the obtained sodalite contains some defects. On the contrary, the ^{29}Si MAS NMR spectrum of the HCl-treated sample is broader, implying that both Q^3 and Q^4 sites are not single environments.[8] The calcined product obtained from the HCl-treated sample displays a broad Q^4 signal (characteristic of amorphous silica), suggesting that the condensation between the Q^3 units occurred upon calcination but the condensed ones were atomically disordered.

Interestingly, the morphology of this new silica sodalite is similar to that of plate-like layered silicate (Figure 2), which is quite different from natural and ever synthesized sodalite. Single crystals of sodalite exhibit morphologies in a cubic symmetry, particularly rhombic dodecahedron, truncated rhombic dodecahedron, and truncated octahedral, while polycrystalline sodalite possesses spherical shapes with several crystal faces.[5,11] Considering the structure of RUB-15 and the XRD pattern showing the strongest peak arising from the (110) plane of sodalite, due to the sample orientation on the XRD holder, the largest face of the crystals is identified as the (110) plane.

Upon calcination, conversion of the AcOH-treated silicate into the sodalite was monitored by in situ powder XRD and by thermogravimetry (TG) equipped with mass spectrometry (MS).[8] The XRD patterns show that the structure is gradually changed over 170 °C. The peaks arising from sodalite are clearly observed over 200 °C and become gradually stronger. The MS spectra reveal that water is a main product of the calcination process up to 300 °C. These results suggest that the condensation of the layered silicate occurred before the decomposition of AcOH. Interestingly, TG and MS results show that the decomposition of AcOH occurs in a wide temperature range (350−800 °C), and differential thermal analysis (DTA) does not display any sharp peaks (data not shown), which is dissimilar to SDAs occluded in other zeolites. After heating the AcOH-treated sample at 800 °C for 3 h, the TG weight is almost constant,[8] indicating that no organic matter was occluded in the sodalite.

The absence of residual species was also confirmed by elemental analysis; the carbon residual was only 23 ppm. The accessibility of the sodalite cage through micropores was investigated by H$_2$ adsorption. Uptakes up to 0.13 wt % were obtained at 303 K and
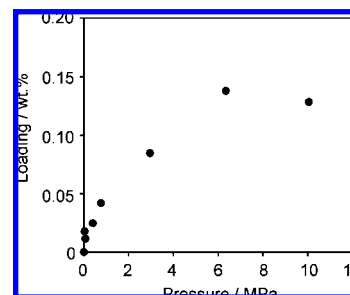
Figure 3. Hydrogen adsorption isotherm on the calcined sample at 303 K.

10 MPa (Figure 3), which is consistent with the simulation results (0.08 wt % at 573 K and 10 MPa).[12] Some of the H$_2$ might be adsorbed onto the defect sites.

In summary, novel silica sodalite without occluded organic matters has been synthesized for the first time by topotactic conversion of layered silicate precursors. The accessible micropores have been confirmed by physical adsorption of hydrogen molecules. Attempts to decrease defect sites by post-treatments of the obtained sodalite are in progress. This plate-like silica sodalite would be very promising as fillers in mixed-matrix membranes for hydrogen separation as well as a model material for studying gas adsorption in the sodalite cage.

Supporting Information Available: Experimental details, crystal structure of RUB-15, ex-situ and in situ XRD patterns, solid-state NMR spectra, and TG-MS results. This material is available free of charge via the Internet at http:// pubs.acs.org.

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