Formation of Si, Al Solid Solution in the Sodalite Framework and Its Characterization

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A formation of complete solid solution series of Si,Al in the sodalite framework was tried in a non aqueous solution. Two types of solid solutions could be successfully prepared. The one was in the region of Si/Al ratio from ∞ to 1.4, and the other from 2.0 to 1.0. The former was assigned as type A, while the other type B. Their X-ray powder diffraction, thermoanalysis and ^{29}Si NMR data were characterized.

It is very difficult to find a complete solid solution of Si,Al in the zeolite framework. Only one reported is the faujasite series including Zeolite X and Y. Most of sodalite samples which occur in nature are 1.0 in the Si/Al ratio. However, Bealocher et al.[1] reported the synthesis of sodalite of Si/Al = 5.0 using TMAOH(Tetramethyl ammonium hydroxide) as a template, while Bibby et al.[2] showed the preparation of pure silica sodalite in ethylene glycol solvent. These results suggest a possibility of formation of solid solution in the sodalite series. In this paper, a systematic preparation of these sodalite series in a non aqueous solution, and their characterization by X-ray diffraction and ^{29}Si NMR spectroscopy are reported.

Both solid NaOH pellets and metallic Al powders were added in the ethylene glycol solvent, and heated at 200 ℃ for 2 days in a Teflon coated reaction tube. After confirming the complete solution of Al metals, a homogeneous gel was prepared by adding fumed silica, and heated at 200 ℃ for one week in the reaction tube. X-ray structures of products were examined by X-ray powder Rietveld analysis, Si/Al ratios by EPMA, local ordering of Si,Al in the framework by ^{29}Si NMR, and thermochemical properties by DTA and TGA.

Any deviations from its intrinsic cubic crystal system was not able to be noticed on the X-ray diffraction patterns. Based on the indexing of cubic symmetry, the lattice parameters were refined by least squares refinement. Figure 1 showed the relationship between the lattice constants and Al contents in the framework. From the figure, continuous solid solutions of Si,Al seemed to be formed in the framework, but some discontinuous points could be noticed at the Si/Al = 1.4, 2.0 and 5.0. Based on a simple criterion introduced here, synthetic sodalites ranging from Si/Al ratio from ∞ to 2.0 were assigned as type A, while those from 1.4 to 1.0 as type B. Sodalites ranging from Si/Al ratio 2.0 to 1.4 were mixtures of both types. Typical X-ray powder diffraction patterns were shown in Figure 2. The type A could be characterized with the presence of its peculiar X-ray

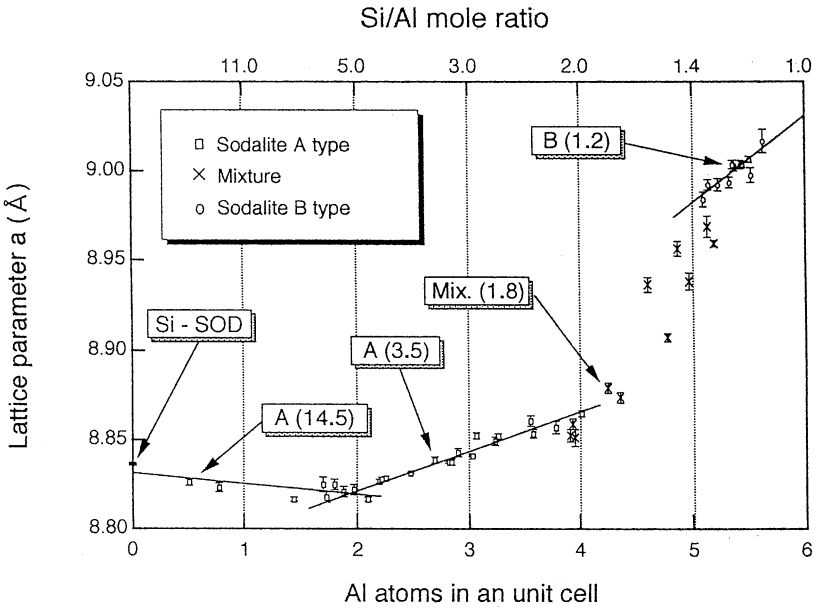

Figure 1. Lattice parameter vs. Al atoms in the unit cell.

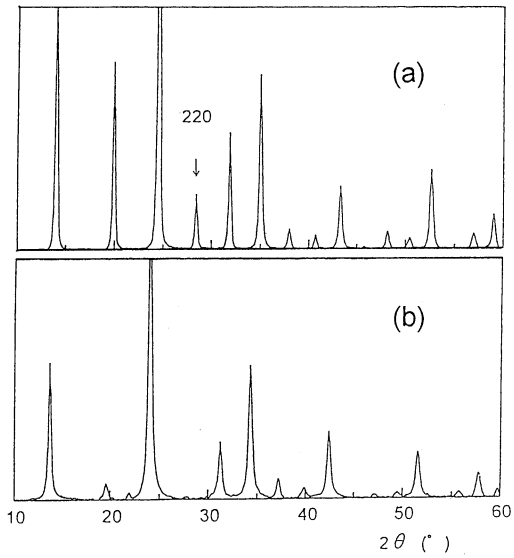

Figure 2. Typical X-ray patterns of synthetic sodalites. (a) Type A (Si/Al=4.71) (b) Type B (Si/Al=1.26) CuKα radiation.

reflection of 220 (3.13 Å), while the type B the absence of it. The chemical compositions of typical samples were determined to be $Si_{12}O_{24}$2.0E.G. for silica sodalite, $Na_{2.6}(Si_{9.9}Al_{2.1}O_{24})(OH)_{0.5}$ 1.7E.G. for type A, and $Na_{7.6}$ $(Si_{6.7}Al_{5.3}O_{24})(OH)_{2.3}$ 1.0E.G. for type B, where E.G. indicates the template ethylene glycol.

By heating the samples in air, the templates included in the cage were easily desorbed to show intrinsic exothermic peaks at different temperatures. For example, Al-free silica sodalite had its strong exothermic peak at 470 ℃, while Al containing type A, and around 410 and 500 ℃ in the type B.

^{29}Si NMR spectra were examined on some typical samples of their Si/Al ratio = ∞, 9.68, 5.09, 2.87, 1.81, 1.29, and 1.08 respectively, which were shown in Figure 3. Deconvoluting the patterns into individual components of Si(4Al), Si(3Al), Si(2Al), Si(1Al), Si(0Al), estimating their intensities and plotting them against Al contents in the framework, it could be certainly realized that there were three inflection points at Si/Al = 4.0, 2.0 and 1.5. These points were completely consistent with those predicted on the SCCL (Substituted Concentric Cluster) theory by Sato.[3] This means that the local Al distribution in the framework is obeyed by Dempsey rule,[4] i.e., minimum number of Al-Al pairs in the 2nd neighbor.

Crystal structures of both type A and type B were examined by X-ray powder Rietveld analysis. There were no differences of fundamental frameworks between them, but the bond distances of T-O and the bond angles T-O-T were remarkably changed with increasing Al contents in the framework. For example, the T-O bond distance of 1.589 Å for Al-free sodalite changed 1.621 Å in the type A (Si/Al = 4.9), and 1.582 and 1.766 Å in the type B (Si/Al = 1.3). Similarly, the bond angles were changed to be 158.3,148.8 and 143.4° in the order listed above. The behavior

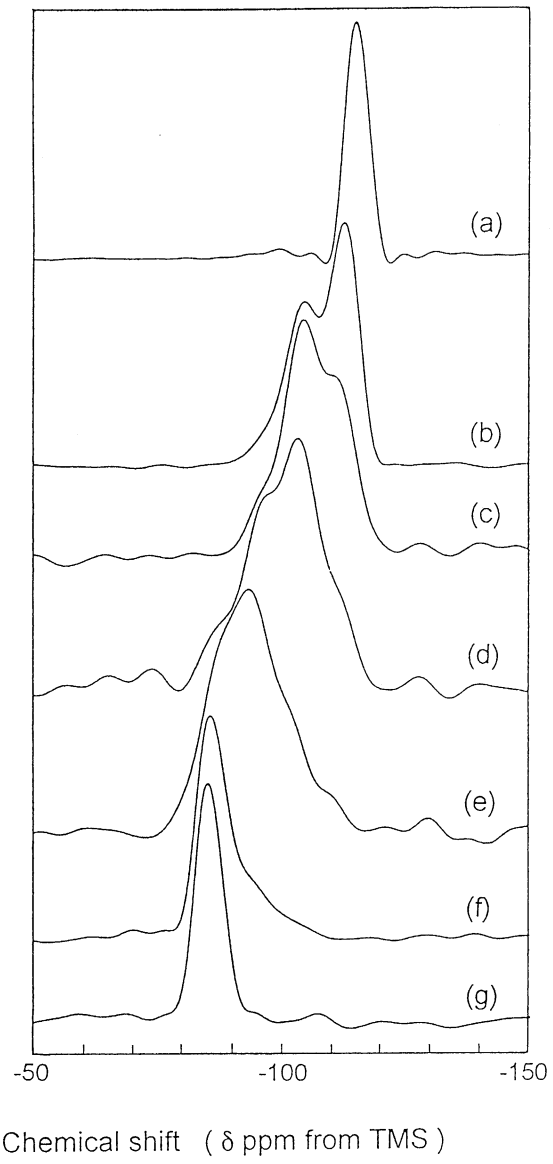

Figure 3. ^{29}Si MAS NMR spectra of synthetic sodalites. Si/Al ratios are (a) ∞, (b) 9.68, (c) 5.09, (d) 2.87, (e) 1.81 (f) 1.29, and (g) 1.08 respectively.

of characteristics 220 reflection was found to be closely related to the evolution of T-O-T angles. The possible trans, cis and gauche conformations of ethylene glycol were examined in the sodalite cage.

References and Notes

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