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Ordered distribution of aluminum atoms in analcime

Abstract Based on the connectivity relations among tetrahedron sites and the NMR spectra, we propose an ordered distribution of aluminum atoms in the framework of analcime with space groups of Pbcb and Pcaa. The symmetries of the ordered distributions are formally the same as Pcca. These symmetries are much lower than those reported by others such as Ia3d, I41/acd, Ibca, and I2/a. The lowering of symmetry results apparently from the fact that aluminum atoms in the framework of analcime were strictly discriminated from silicon atoms. Dependence of the populations of Si($n$Al)$_s$ upon Al content was estimated from $^{29}$Si MAS NMR, and can be successfully simulated by the ordered distributions. In the simulation, a small number of defects in the Al distribution were introduced into the ordered distribution mainly to adjust the deviation of Al content per unit cell from the typical composition. Analysis of the powder X-ray diffraction patterns of analcime was carried out, which suggests that the space groups proposed in the present work offer a better fit than the ones reported previously.

Key words Zeolite · Analcime · Structure · Aluminum distribution

Introduction

Aluminum distribution in a zeolitic framework plays an important role in the physicochemical properties of zeolite. The ordering of Al atoms in zeolitic frameworks is of general interest. Most studies concerned with this problem have indicated that Al atoms are located at a given site in a random manner because no direct method for determining the ordered distribution exists. For example, in X-ray diffraction study, the concentration can be learned in a given site only from the average bond length between the atoms in tetrahedron (T) sites (Si or Al) and the oxygen atom (Jones 1968) (abbreviated as T-O bond length). On the other hand, the population of Si atoms in Si(-OAl)$_n$(-OSi)$_4$ (where 0 ≤ $n$ ≤ 4, and Si(-OAl)$_n$(-OSi)$_4$ are abbreviated as Si($n$Al) hereafter) can be obtained by the solid-state NMR spectra of $^{29}$Si (Lipmaa et al. 1981; Engelhard and Michel 1987; Klinowsky 1993). We can only determine the average number of the Al atoms adjacent to the Si atoms via oxygen atom from this measurement. The overall ordered distribution of the Al atoms in the framework remains unknown. The two-dimensional solid-state NMR technique (Fyfe et al. 1991) has recently been developed, but the technique does not allow analysis of the degree of ordering of the AI distribution. Due to these mentioned experimental limitations, most workers still assume that the Al atoms are randomly distributed in the zeolitic framework, except for special cases such as natrolite (Lipmaa et al. 1981).

Analcime is one of the cases, for which the order of Al atoms in the framework has been studied by NMR and XRD studies (Murdoch et al. 1988; Phillips and Kirkpatrick 1994; Mazzi and Galli 1978). The framework structure was first proposed by Taylor (1930) with a cubic space group Ia3d by XRD. He assumed that the Al atoms were randomly distributed in the T sites. After Taylor’s (1930) work, Knowls et al. (1965) and Ferraris et al. (1972) analyzed the structure with the same space group. Mazzi and Galli (1978) have also analyzed with a tetragonal space group I4$_1$/acd and orthorhombic Ibca. Similarly, Pechar (1988) studied the problem with monoclinic I2/a. They concluded that the Al atoms were concentrated only at certain T sites, but considered that the Al atoms were randomly distributed at these sites.

The ordering of Al atoms in analcime framework has been studied by Murdoch et al. (1988), Teerstra et al. (1994), Phillips and Kirkpatrick (1994) and Kohn et al. (1995) using solid-state NMR technique. Murdoch et al. (1988) concluded that the Al atoms are concentrated at T$_2$ site for one sample and at T$_1$ and T$_3$ sites for another sample. They have also suggested that the Al atoms are...
randomly located at these sites. Teerstra et al. (1994) and Kohn et al. (1995) have also mentioned the concentration of Al atoms at certain sites. Phillips and Kirkpatrick (1994) suggested that the Al ordering is preferred to random distribution from the entropy viewpoint. These data also lead to the estimation of the ordered distribution of Al atoms in the framework.

Recently we proposed a method for determining the ordered distribution of Al atoms in the zeolitic framework (Takaishi and Kato 1995), and have analyzed the ordered distribution of Al atoms in some zeolites (Takaishi and Kato 1995; Takaishi et al. 1995; Kato et al. 1996). In these studies, candidates of the ordered distribution of Al atoms in a zeolitic framework were searched, based on the connectivity relation between T sites and the Al-O-Al linkage avoidance rule (the Loewenstein rule (Loewenstein 1954)). The distribution of Al atoms in zeolite samples was determined by considering the observed population of [Si(nAl)], T-O bond length, location of the extraframework cation and so on. These studies showed that the number of configurations, which satisfy both the framework topology and the NMR spectra, is a very small number and often unique.

In the present study, we investigated the ordered distribution of Al atoms in the framework of analcime. The composition of analcime is reported as (K,Na)Al6Si31.6O96 · 15.7H2O, and the number of Al atoms per unit cell, x, is 13.4 < x < 16.1 and typically 16 (Gottardi and Galli 1985). Pechar (1989) and Coombs and Whetten (1967) have reported analcime containing more Al atoms in the framework, which seems to be only in some rare cases. The fact that the Al content per unit cell is restricted in a narrow region suggests that the distribution of Al atoms is ordered in the frameworks of zeolites, such as natrolite. We have also developed a method for a systematic analysis of the dependence of the [Si(nAl)] population on the Al contents based on the ordered distribution, and examined the validity of the ordered distribution by the Rietveld analysis of the powder X-ray diffraction pattern.

Results and discussion

Ordered distribution of the Al atoms

A connectivity table (Table 1) of T sites on the basis of connectivity relations between T sites was made as described in Takaishi and Kato (1995). The framework of analcime contains 48 T sites. The atomic coordinates of the sites were derived from the asymmetric unit (0.662, 0.588, 0.125) assuming the cubic space group Ia3d. The order of the sites in the connectivity table corresponds to the number of the equivalent positions represented in the International Table for Crystallography, vol A (Harn 1995).

Using the connectivity table, possible configurations of Al atoms in the framework of analcime can be searched under the restriction of Loewenstein’s rule. In a typical case where 16 Al atoms are distributed in the 48 T sites of analcime, about 2770000 configurations of Al distribution were obtained. It was also found that the maximum number of Al atoms is 24 per unit cell in the framework, precisely half the number of T sites.

Next, candidates of the ordered distribution were searched from these configurations on the basis of the population of [Si(nAl)]s. Configurations having seven patterns of [Si(nAl)] populations were selected (Table 2). These patterns resemble the pattern of sample C whose chemical composition is close to the typical composition. The results are summarized in Table 2 along with their chemical composition. The configurations with population pattern VII, i. e. [Si(4Al)] = [Si(0Al)] = 0, [Si(3Al)] = [Si(1Al)] = 8, and [Si(2Al)] = 16, have the highest symmetry of orthorhombic space group Pbcn or Pca21 (both of them formally belong to space group Pcca). It is assumed that these configurations with space group Pcca are the ordered distribution of Al atoms because the distortion, introduced by the difference of atomic radii between Al and Si atoms, is relieved in the frameworks.

Experimental

Materials

Samples of analcime were synthesized by Mizusawa Industrial Chemicals Ltd (Nakazawa et al. 1992). The sample compositions determined by chemical analysis are Na17.3Al17.3Si30.7O96 · 15.5H2O (sample A), Na16.4Al16.4Si31.4O96 · 15.7H2O (sample C), Na14.4Al14.4Si33.6O96 · 16.1H2O (sample D) and Na13.8Al13.8Si34.2O96 · 16.9H2O (sample E). The sample compositions determined by chemical analysis are Na18.3Al18.3Si29.7O96 · 16.3H2O (sample A), Na17.3Al17.3Si30.7O96 · 15.5H2O (sample B), Na16.4Al16.4Si31.4O96 · 15.7H2O (sample C), Na14.4Al14.4Si33.6O96 · 16.1H2O (sample D) and Na13.8Al13.8Si34.2O96 · 16.9H2O (sample E). The sample purity was investigated by XRD, and confirmed that there were no peaks resulting from impurities.

Samples for the XRD measurements were dehydrated by heating at 400°C for 2 h and cooled to room temperature before XRD measurement to remove the effects of the extraframework water molecules and decrease the number of fitting parameters in the Rietveld analysis. Sample preparation and measurement were made in a medium of dry helium gas.

Synthesized samples for the NMR measurements were used without any further treatment.

Apparatus

Varian Unity-400 plus NMR spectrometer was used with a pulse width of 5.5 μs (π/4 pulse), a pulse interval of 20 s, an observing frequency of 79.4586 MHz, and a spinning rate of 6 kHz. A thousand FIDs were stacked. Samples were introduced in a 7 mm spinner. Silica nitride from the spinner was employed as a secondary standard of chemical shift (~50.1 ppm from tetramethylsilane).

Powder X-ray diffraction patterns were collected by MXP18 (Mac Science Co.) with a graphite monochrometer using fixed time methods. An X-ray tube with a copper target was operated at 20 kV, and the tube current was adjusted to such an extent that the maximum peak intensity became about 5000 counts. The widths of the divergence slit, scattering slit and receiving slit were 0.5°, 0.5° and 0.15 mm respectively. The step width (2θ) was 0.05° and the fixed time was 10 s.

Rietveld refinements of X-ray diffraction profile were carried out with a computer program named RIETAN (Izumi 1985). The initial lattice constants and atomic coordinates for the space group Ia3d were employed from the data determined by Ferraris et al. (1972). The initial values for the different space groups were deduced from the results obtained from the analysis with space group Ia3d.