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The Crystal Structure of Ion-exchanged Mordenite

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Synopsis. The crystal structure of hydrated mordenite, yielded at Hokiyadake, Nagano City, Japan, $Na_{1.4}Ca_{2.9}Al_{7.2}Si_{40.8}O_{96} \cdot nH_2O$, were refined to R=0.070 for 1526 observed reflections. Notable ordering of the aluminum positions of the aluminosilicate framework was observed.

Study of the location of aluminum atom in mordenite provides a basis for the interpretation of its catalytic properties. All structure determinations for mordenite so far reported have been done on a specimen from Challis Valley, Idaho.[1-2] The structure revealed the weak electron density peaks other than the Cmcm stacking. Here we report the structure of another mordenite obtained at Hokiyadake, Nagano City, Japan, which has a distinct ordering of aluminum atoms in the $AlSi_5O_{12}$ silicate framework. The calcium atoms populated as dominant cations in this mordenite.

Experimental

Single crystals of natural mordenite from Hokiyadake, Nagano City, Japan were ion-exchanged with 1 M HCl solution at room temperature for 24 h, yielding the composition, $Na_{1.4}Ca_{2.9}Al_{7.2}Si_{40.8}O_{96} \cdot nH_2O$ from atomic absorption and ICP spectrometry. A needle crystal with dimensions of 0.20×0.08×0.06 mm was used for the X-ray measurements. The crystal data are: $Na_{1.4}Ca_{2.9}Al_{7.2}Si_{40.8}O_{96} \cdot nH_2O$, orthorhombic, Cmcm, a=18.089(3), b=20.412(4), c=7.504(1) Å, U=2771(2) Å^3, d_m=1.80 g cm^{-3}, $\mu(\mathrm{Mo}\,K\alpha)$=7.88 cm^{-1}, $\lambda(\mathrm{Mo}\,K\alpha)$=0.7107 Å. Intensity data were collected on a Rigaku AFC-5 automated four-circle diffractometer with graphite monochromator up to 2θ=60°. Cell parameters were refined by a least-squares method on the basis of 15 2θ values for Mo $K\alpha$ radiation ($20° < 2\theta < 40°$). 1526 unique reflections with $|F_o| > 3\sigma(|F_o|)$ were measured. No absorption correction was made. Cations and water molecules were located and the structures were refined by the alternating use of least-squares and Fourier methods, the UNICS-III computation program system[3] being employed. Final R value for the hydrated sample is 0.070 for 1526 observed reflections. In the final cycle $(\Delta/\sigma)_{max}$ was 0.2 for the x coordinate of O(6). No peaks higher than 0.35 e Å^{-3} were observed in the final difference density map. Complex neutral atom scattering factors from the International Tables for X-Ray Crystallography[4] were used. Table 1 gives the positional parameters for the silicate framework atoms and the cations.*

Results and Discussion

Interatomic distances and bond angles in the mordenite framework are listed in Table 2. The fundamental framework showed no stacking faults in contrast to the previous results reported by Mortier *et al.*[2] Chemical analysis showed that Ca^{2+} and also Na^+ remained in spite of prolonged ion-exchange by 1 M HCl (1 M=1 mol dm^{-3}) and that the former dominates by far over the latter. Therefore, extra framework electron densities were assigned to Ca^{2+}, Na^+, and orderly adsorbed water molecules. Ca^{2+} is located at the center of the six-membered rings, whereas the cation in the main channel is ascribed to Na^+ since the former

Table 1. Positional parameters (×10^4) and equivalent isotropic temperature factors $B_{eq}=4/3\sum_i\sum_j\beta_{ij}a_ia_j$.[5]

	x	y	z	B_{eq}/Å^2
T1(AL)	2008(1)	4279(1)	5413(3)	0.9
T2(AL)	1959(1)	1915(1)	5461(3)	1.1
T3(AL)	873(1)	3854(1)	2500	0.8
T4(AL)	859(1)	2278(1)	2500	0.8
01	1250(3)	4188(3)	4322(9)	2.7
02	1230(3)	1945(3)	4241(9)	2.7
03	2642(4)	3774(3)	4835(10)	3.9
04	955(4)	3057(4)	2500	3.3
05	1674(4)	1964(5)	7500	3.2
06	1821(4)	4212(5)	7500	2.5
07	2346(5)	5000	5000	2.2
08	2500	2500	5000	4.5
09	0	4114(6)	2500	2.0
010	0	2051(6)	2500	1.9
CA	0	5000	0	3.9

Table 2. Interatomic distances and bond angles in the mordenite framework

T1-01	1.609(5)	03-T1-01	112.9(3)	T1-01-T3	144.9(3)
T1-03	1.616(6)	03-T1-06	111.1(4)	T2-02-T4	145.0(3)
T1-06	1.610(2)	03-T1-07	104.8(3)	T2-03-T1	157.5(6)
T1-07	1.625(3)	01-T1-06	107.9(3)	T4-04-T3	168.7(5)
		01-T1-07	109.6(3)	T2-05-T2	143.1(7)
mean	1.615 Å	06-T1-07	110.7(3)	T1-06-T1	153.1(6)
				T1-07-T1	135.6(7)
T2-02	1.606(5)	mean	109.5°	T2-08-T2	180.0(5)
T2-03	1.588(5)			T3-09-T3	145.0(6)
T2-05	1.610(3)	08-T2-02	110.5(2)	T4-010-T4	146.8(6)
T2-08	1.583(2)	08-T2-03	107.7(4)		
		08-T2-05	110.8(3)	mean	152.0°
mean	1.597 Å	03-T2-02	109.6(5)		
		03-T2-05	109.6(5)		
T3-01	1.664(5)	02-T2-05	106.4(3)		
T3-04	1.639(7)				
T3-09	1.656(4)	mean	109.0°		
mean	1.656 Å	01-T3-01	109.8(3)		
		04-T3-09	112.5(4)		
T4-02	1.620(5)	04-T3-01	111.4(2)		
T4-04	1.588(7)	09-T3-01	105.7(3)		
T4-010	1.616(3)				
		mean	109.4°		
mean	1.611 Å				
		02-T4-02	108.1(3)		
		04-T4-010	112.9(4)		
		04-T4-02	111.6(2)		
		010-T4-02	106.2(3)		
		mean	109.4°		

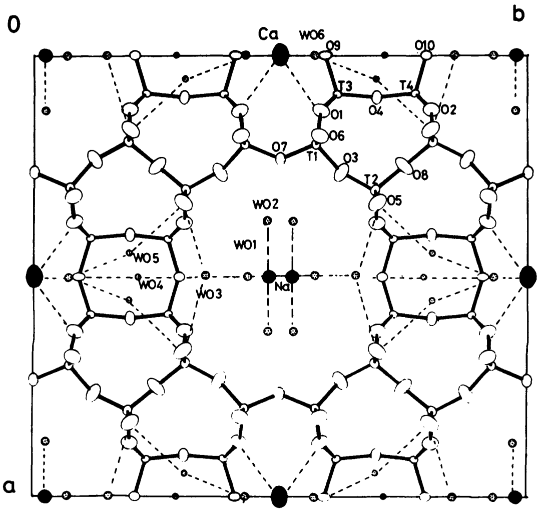

Fig. 1. The crystal structure viewed down along the c axis. WO stands for ordered water molecule.

electron density exceeded by far than the latter.

The T(Si or Al atoms)–O distance was influenced by the Si and Al contents and their positions in the framework. The overall mean T–O distance of 1.620 Å compares well with the typical values for the mordenite as shown in Table 2. The mean T3–O distance, 1.656 Å, is longer than the other T–O distances, which is suggestive of more probable accumulation of the aluminum atoms on the T3 site than on the remaining three. Figure 1 shows the crystal structure viewed down along the c axis. The Ca^{2+} at (0, 1/2, 0) was not exchanged by 1 M HCl. This is explained by the existence of ordered AlO_4^- tetrahedra at T3 site. The larger charge 2+ of Ca^{2+} rather than Na^+ could favor the charge compensation of AlO_4^-. The presence of the mirror plane (100) in Cmcm may lead to unfavorable charge distribution of the neighboring AlO_4^- tetrahedra. Thus, Al(T3) and adjacent symmetry related Al(T3′) atoms might be statistically disordered, and the space group Cmcm adopted in the present investigation represents a pseudo-symmetry.

The structure for dehydrated mordenite was also determined. The cell dimensions reduced to a=17.941(4), b=20.276(6), c=7.482(2) Å by dehydrating a capillaried sample at 10^{-5} Torr and 350 °C for 48 h. During dehydration the Na^+ remaining in the center of the large channel, which occupied the two positions at random near the center, moved to the side wall of the main channel, and the T3-09-T3′ angle changed by up to 8.1 ° (1.4 °) with mean change of 2.2 °. The remarkable ring puckering of the framework skeletons reduced the symmetry from Cmcm to the lower space group.

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