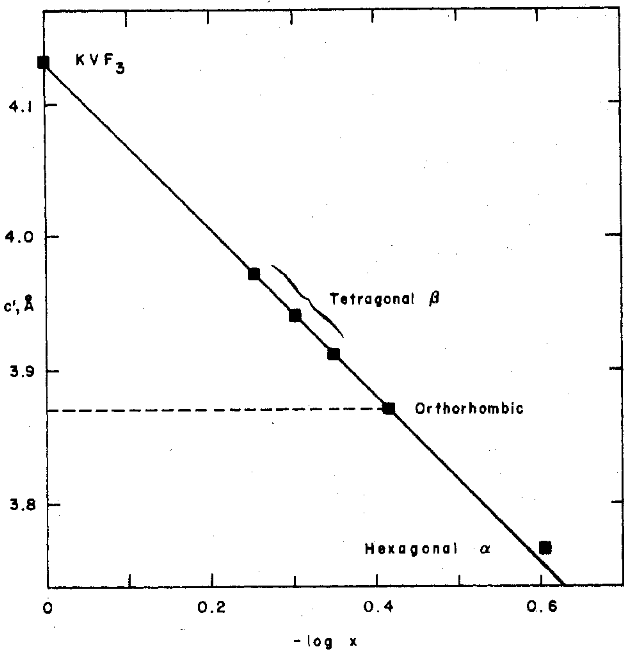

Figure 2. Linear plot of (−)log x vs. interlayer distance c' of K_xVF_3 compounds.

layers, as the hexagonal and tetragonal phases do, and that it is probably a compound of fixed composition.

The magnetic susceptibility measurements of the tetragonal phase indicate that antiferromagnetic ordering occurs at about 45 K. The values of Θ, C_M, and T_N are not very sensitive to composition. The shapes of the χ_M^{-1} vs. T plots, however, show that the nature of the ordering changes significantly with changes in x. From these plots, it appears that as x approaches the theoretical limit of 0.6, the ordering approaches classical antiferromagnetic behavior. In the tetragonal K_xWO_3 structure, space group $P4/mbm$,[2] there are two distinct lattice positions occupied by the smaller cations. These are the 2(c) and 8(j) sites. Buchanan[8] and Banks[6] independently established by Mössbauer that in tetragonal K_xFeF_3, the 2(c) sites are preferentially occupied by Fe(II), whereas, the 8(j) positions are occupied by both Fe(II) and Fe(III). If this condition prevails in K_xVF_3, the magnetic tendencies observed can qualitatively be explained. If the 2(c) sites are only occupied by V(II) ions, as x approaches 0.6, the ratio of V(III):V(II) on 8(j) sites approaches 1. This suggests that in the magnetically ordered state there is antiferromagnetic ordering of V(II) ions within 2(c) sites and of V(II) and V(III) ions within 8(j) sites such that no resultant ferromagnetic moment is observed. As x decreases, however, the tendency toward ferrimagnetic behavior is probably a consequence of the ratio of V(III):V(II) on 8(j) sites increasing toward the maximum possible value of 3 at the theoretical limit of x = 0.4. The fact that T_N does not change significantly with x is a fair indication that the overall ordering mechanism is also independent of x. The possible magnetic structures of these compounds are exciting and the observed effects are almost certain to be field dependent. Further studies are necessary to understand this system completely.

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Registry No. KVF_3, 27498-34-6.

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Crystal Chemistry of Dealuminized Mordenites

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Unit cell dimensions have been determined for dealuminized NH_4 mordenites having SiO_2/Al_2O_3 ratios of 10–100. The lattice contractions which occur on aluminum removal are strongly anisotropic and nonlinear. An explanation for the differing dependence of the a, b, and c parameters on the SiO_2/Al_2O_3 ratio is proposed in terms of aluminum site distribution within the as-synthesized zeolite, there being three basic types of siting in the mordenite structure. Strong additional effects are observed where ammonium is replaced by sodium or by hydronium ion, effects attributed to the smaller size of these latter species.

Introduction

Mordenite is both a naturally occurring and a synthetic zeolite, with an idealized composition of $Na_8Al_8Si_{40}O_{96}\cdot 24H_2O$. Its structure, solved by Meier,[1] is orthorhombic with cell parameters of a = 18.11, b = 20.53, and c = 7.528 Å in the sodium form.[2] The structure is derived from interconnected chains of SiO_4 and AlO_4 tetrahedra whose projection along the c axis is shown in Figure 1. It possesses large, 12-ring pores parallel to [001], linked by 8-ring tortuous channels about [010].

Both naturally occurring and synthetic mordenites vary only slightly in chemical composition. On the basis of x-ray diffraction and elemental analysis data on 35 natural samples, Passaglia reported a range in the $SiO_2/(Al_2O_3 + Fe_2O_3)$ ratio

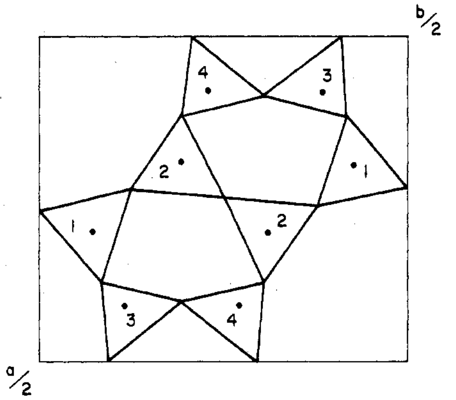

Figure 1. Projection of the mordenite framework along [001].

of about 8–11.[3] Sand, in his successful preparation of "large-port" mordenite, a mordenite possessing the sorptive properties expected for the 12-ring pore system, obtained samples only in the composition range of SiO_2/Al_2O_3 = 9–10,[4] a narrow range confirmed by several other investigators.[5] There exists of course no evidence that mordenites will not be crystallized in a broader composition range, and indeed a synthesis of siliceous mordenites, having apparent SiO_2/Al_2O_3 ratios as high as 20, has been reported.[6] The narrow range commonly observed, however, has been taken as evidence for the possible ordering of aluminum within the structure.[1]

"Siliceous" mordenites can be readily prepared by removal of framework aluminum, either by acid extraction[7-9] or by combined thermal and acid treatments.[10,11] Both techniques, when carefully employed, can effect about 80% dealuminization without significant loss in crystallinity. Further removal of aluminum becomes increasingly difficult and apparently requires the combined, thermal cycle.

X-ray diffraction provides the most direct measure of structural differences between mordenite samples of varying framework composition. Among natural samples, a negative correlation in the *b* parameter was found as the silicon occupancy of the framework tetrahedra increased from 80 to 85%.[3] No detailed x-ray examination of dealuminized mordenites has been published, but several studies have noted a general contraction in the unit cell as aluminum was removed from the zeolite structure.[7-9,11]

In the present study the variation in each of the three unit cell dimensions has been determined for a series of dealuminized mordenites of SiO_2/Al_2O_3 = 10–100, all in the ammonium form. The implications of the results on aluminum distribution in mordenites are discussed, and the sensitivity of the lattice parameters to specific cation effects is briefly examined.

Experimental Section

Materials. The initial mordenite samples used in these experiments were obtained from Norton Co. as fine crystalline powders and are designated as follows (SiO_2/Al_2O_3 ratios in parentheses): Na-Mord (10.9), Na-Mord (12.1), H-Mord (13.9), H-Mord (15.0), and H-Mord (93).

Aluminum was removed from the various samples by refluxing in hydrochloric acid solutions of concentration 0.1–6 M, unless otherwise noted. In a typical dealuminization experiment, 200 g of H-Mord (13.9), containing 0.34 mol of aluminum, was refluxed for 2 h in 800 ml of 3 M HCl (2.4 mol). The solution was filtered, washed well to remove any excess acid or aluminum species, and treated with NH_3 gas. Any residual sodium was removed by exchanging with 1 l. of 2 M NH_4NO_3 (and 0.02 M NH_4OH), at reflux, for 2 h. After being filtered and washed, the sample was boiled 2 h in 1 l. of water to remove any physically sorbed excess ammonia or any remaining NH_4NO_3.

Samples were analyzed in duplicate for sodium, silica, and alumina in Mobil's Paulsboro Laboratory. All samples were analyzed for NH_4 content by calcination in dry helium to 1000 °C and titration of evolved NH_3 with sulfamic acid, in a technique adapted from Kerr and Chester.[12] Calcination was effected in a Du Pont 951 thermogravimetric analyzer; ammonia analysis, with a Radiometer automatic titrator attached to the tga effluent gas stream. Both sodium and ammonia analyses on the acid-extracted samples confirmed that the exchange procedures were at least 95% effective in producing the ammonium form of the zeolite (based on an expected NH_4/Al ratio of one).

Where sodium-form mordenites were studied, samples either were as-synthesized or were exchanged from the NH_4 form. Refluxing 20 g of ammonium mordenite with 200 ml of 2 M $NaNO_3$ twice, 4 h, was sufficient to replace >95% of the ammonium cations with sodium. Hydronium-form samples were studied without intermediate ammonium exchange.

X-Ray Measurements. A Siemens x-ray diffractometer equipped with scintillation counter, pulse height analyzer, strip chart recorder, and step-scanning accessory was used in the present experiments. All samples were equilibrated for at least 16 h in a 51% relative humidity constant-humidity cabinet prior to examination. Crystallinities were determined by comparing the sum of the peak heights of the [330], [150], [202], [350], and [402, 332] reflections (19–31° 2θ) with that for NH_4-Mord (10.9), scanning at 0.5°/min. Unless noted, all crystallinities exceeded 90%. Line widths were measured at half-height on the [680], [1000], and [882] reflections, scanning at 0.02°/min, and showed no variation with SiO_2/Al_2O_3 ratio.

Lattice parameters were determined in the presence of 5–10% silicon powder internal standard (Alfa Inorganics). Samples were step-scanned at 0.02°/min, and Cu Kα_1 reflections were determined either from the peak intensity or from the strip chart plots. Eight reflections (43–61° 2θ) were normally used in the determinations: [0100], [680], [004], [713], [1000], [534], [843], and [882], reflections identified overwhelmingly with a single *hkl* set. S. L. Lawton of Mobil's Paulsboro Laboratory provided the data necessary for selecting the reflections. The unit cell parameters were calculated by simultaneous solution and averaging of all possible permutations of the eight *d* spacings corresponding to these reflections. Standard deviations for a set of calculations averaged about 0.005 Å.

Table I. Mordenite Compositions and Preparations

Sample (SiO_2/Al_2O_3)	Al/uc	Starting material (SiO_2/Al_2O_3)	Prepn method[a]
Mord (11.1)	7.36	NaZ (10.9)	NH_4 exchanged
Mord (12.4)	6.67	NaZ (12.1)	NH_4 exchanged
Mord (13.0)	6.38	NaZ (12.1)	0.1 N HCl, 15 min, reflux
Mord (13.6)	6.15	NaZ (10.9)	1 N HCl, 15 min, reflux
Mord (14.2)	5.91	HZ (15.0)	NH_3 gas, NH_4 exchanged
Mord (14.5)	5.84	HZ (13.9)	NH_3 gas, NH_4 exchanged
Mord (14.7)	5.77	HZ (15.0)	NH_3 gas only, no exchange
Mord (16.7)	5.14	NaZ (12.1)	1 N HCl, 15 min, reflux
Mord (16.6)	5.16	HZ (13.9)	600 °C, 20 mm H_2O, 30 min; 0.1 N HCl, 30 min, reflux
Mord (20.3)	4.30	HZ (15.0)	6 N HCl, 1 h, reflux
Mord (20.4)	4.28	HZ (13.9)	3 N HCl, 3 h, reflux
Mord (23.4)	3.79	HZ (15.0)	3 N HCl, 3 h, reflux
Mord (31.8)	2.84	HZ (15.0)	6 N HCl, 2 h, reflux
Mord (33.5)	2.71	HZ (15.0)	3 N HCl, 7 h, reflux
Mord (34.3)	2.65	HZ (15.0)	6 N HCl, 2 h, reflux
Mord (46.0)	2.00	HZ (15.0)	3 N HCl, 24 h, reflux
Mord (46.1)	2.00	HZ (15.0)	6 N HCl, 4 h, reflux
Mord (46.4)	1.99	HZ (15.0)	6 N HCl, 4 h, reflux
Mord (50.1)	1.85	HZ (15.0)	6 N HCl, 6 h, reflux
Mord (59.2)	1.56	HZ (15.0)	6 N HCl, 16 h, reflux
Mord (59.7)	1.56	HZ (15.0)	6 N HCl, 24 h, reflux
Mord (61.2)	1.52	HZ (15.0)	6 N HCl, 8 h, reflux
Mord (65.1)	1.43	Mord (59.7)	600 °C, 20 mm H_2O, 2 hr; 0.1 N HCl, 30 min, reflux
Mord (66.4)	1.41	Mord (59.2)	6 N HCl, 16 h, reflux
Mord (73.0)	1.28	HZ (14.8)	650 °C, 3 h; 0.5 N HCl, 16 h, reflux[b]
Mord (92.9)	1.01	HZ (93)	NH_3 gas, NH_4 exchanged[b]

[a] Unless otherwise noted, all samples were treated with NH_3 and were NH_4 exchanged following dealuminization. [b] 70–80% crystalline.

Table II. Cation Effects on the Unit Cell Dimensions of Mordenites

Cation	Al/uc	Cell constant, Å[a]		
		a	*b*	*c*
Na^+	6.81	18.11	20.48	7.525
NH_4^+	6.67	18.15	20.42	7.504
Na^+	1.52	18.08	20.27	7.470
NH_4^+	1.52	18.08	20.27	7.468
H_3O^+	6.04	18.18	20.33	7.491
NH_4^+	5.91	18.15	20.39	7.498
H_3O^+	1.62	18.09	20.23	7.465
NH_4^+	1.62	18.08	20.27	7.468

[a] ±0.01 Å.

Results

Samples. In Table I are listed the samples investigated, their preparation, and their framework aluminum content. The majority of the samples were prepared by acid extraction for varying time periods, those samples representing the basic series of mordenites examined. Due to literature reports of structural damage by very concentrated acids,[7,11] extraction was limited to ≤6 M acid. Evident from the data in Table I is a limiting behavior in the aluminum removal process, even lengthy extraction being ineffective in reducing the aluminum content of the present starting materials below a value of ~1.5 Al/uc ($SiO_2/Al_2O_3 = 62$). A similar behavior was noted by Chen and Smith in their combined thermal and acid treatments of mordenite samples, the specific limit varying somewhat with the individual mordenite preparation.[11]

In addition to the acid-leached materials, several samples are included in Table I which were prepared by combined thermal cycles or which exhibit reduced crystallinities (70–80%). Inclusion of these samples was necessary in order to determine whether the x-ray results were specific to an individual series of acid-extracted materials or whether they may pertain to dealuminized mordenites more generally.

Cation Effects. The presence of aluminate tetrahedra in a zeolite framework is expected to cause an expansion in the lattice, an expansion associated with the negative charges on those tetrahedra and with the larger size of aluminate as compared with silicate species.[13] Conversely, removal of aluminum results in a contraction.

Cations can have a significant influence on lattice dimensions, as shown in Table II, but these influences decrease with decreasing aluminum (and associated cation) in the framework. As the cation was varied in the sequence $H_3O^+ \rightarrow Na^+ \rightarrow NH_4^+$ for mordenites of similar framework composition, marked, anisotropic shifts in *a*, *b*, and *c* occurred and were attributed to specific, local interactions between cation and aluminate. Such distorting interactions are expected to be most pronounced with the smallest cations, Na^+ and H_3O^+, and would be minimized with the larger ammonium ion. For this reason and for its easy accessibility the NH_4 form was selected for detailed investigation.

Structural Parameters. The variation in the three unit cell dimensions with aluminum content is shown in Figure 2 for this series of zeolite samples. Characterizing the plots are a strong nonlinearity and a pronounced anisotropy in the dependence of *a*, *b*, and *c* on Al/uc. The *a* parameter is essentially unaffected by removal of up to 25% of the framework aluminum, while an exceedingly strong contraction occurs in the *b* direction, tapering off at high SiO_2/Al_2O_3 (~50, or 2 Al/uc).

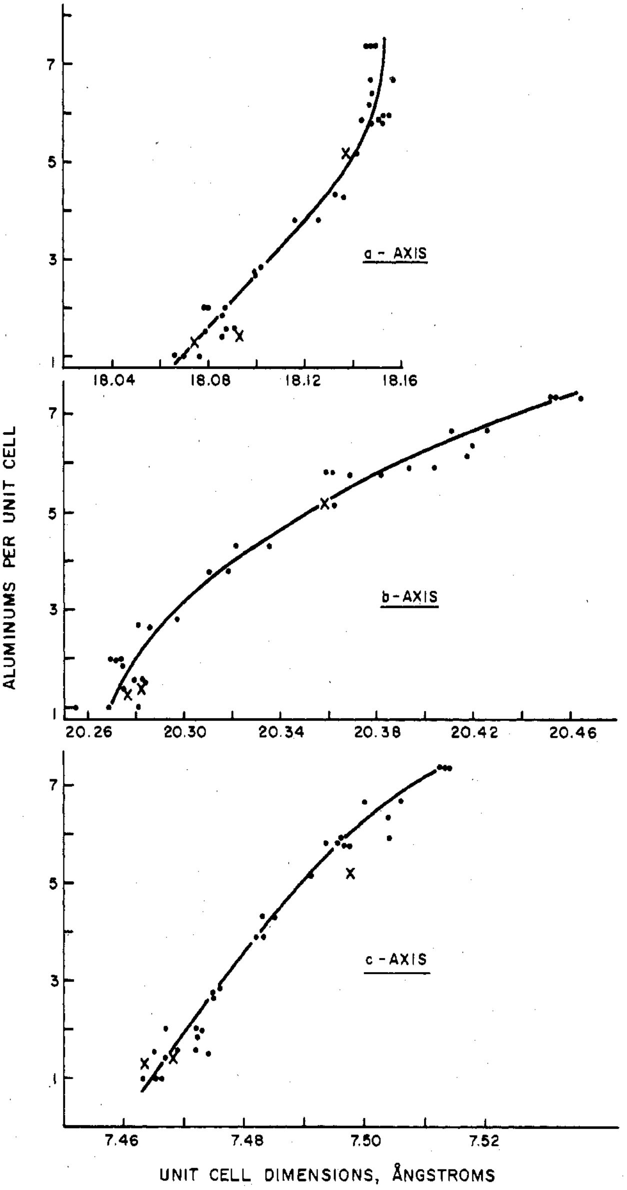

Figure 2. Lattice parameters of dealuminized mordenites: •, acid leached; ×, combined thermal and acid treated.

In addition to the basic set of acid-extracted samples, those materials obtained by thermal cycles and those exhibiting low apparent crystallinities have been included, with special (×) designation, in Figure 2. To within experimental error, the unit cell dimensions of these samples agreed with those of the "standard" series and were a direct measure of the framework composition. Furthermore, no difference in x-ray diffraction data was observed between ammonium mordenites prepared by exchange (as described) and those prepared by simple exposure of a hydronium zeolite to ammonia gas.

Discussion

X-ray powder diffraction patterns yield only averages of the unit cell dimensions of a zeolite, averages which could well be influenced by crystallite inhomogeneity or by partial structural collapse. If, for example, aluminum were preferentially removed from the crystallite exterior, a distribution in unit cell dimensions would result with an accompanying line broadening in the high-angle reflections examined. There was no change either in crystallinity or in line width for the entire series of "standard" samples investigated, exceptions in crystallinity being noted in Figure 2. Thus it was concluded that the trends in lattice parameter truly reflect contractions in the mordenite framework.

Contractions in a structure such as mordenite can arise from either of two causes: from strain or simply from aluminum siting. That the strongly nonlinear and variable contractions

Table III. Bond Distances and Tetrahedral Projections in Mordenite[a]

Tetrahedron[b]	Av T–O, Å	Projection, Å		
		a	*b*	*c*
1	1.622	2.52	2.54	2.41
2	1.607	2.31	2.62	2.43
3	1.639	2.23	2.28	2.70
4	1.625	2.22	2.28	2.65

[a] Taken from ref 2. [b] Designation in Figure 1.

in *a* and *b* are not just artifacts of strain was suggested, although not proven, by the natural occurrence and by the facile synthesis of mordenites of specified composition. Presumably a highly strained material would not persist geologically but would spontaneously expel aluminum, for example. It is proposed then that the contractions directly reflect aluminum removal.

Single-crystal studies of mordenite have shown that the most likely positions for aluminum are 3 and 4, on the basis of bond distance measurements alone.[2] The present data suggest a broader distribution. On the basis of these dealuminization results, it is proposed that aluminum is distributed throughout all three possible sites (1, 2, and 3 + 4) and that the trends in *a*, *b*, and *c* are the result of that distribution.

In Table III are listed the average Si–O (or Al–O) bond distances and the projections onto *a*, *b*, and *c* of the respective silicate and aluminate tetrahedra identified in Figure 1. Among the four possible sites, 2 is noteworthy in its exceptionally short T–O distance (1.607 Å). The average Al–O and Si–O distances in aluminosilicate structures are 1.75 and 1.62 Å, respectively.[13] In view of the data in Figure 2 it is proposed that the short bond distance in the 2 position is a property of the mordenite secondary building unit structure and that any aluminum residing in that position will be preferentially removed by acid treatment. The 2 position has its maximum projection along [010] and its minimum along [100]. If the initial removal of 25% aluminum (down to ~6/uc) were from 2, one would expect a maximum change in *b* and a minimum in *a*, as is indeed observed.

At intermediate levels of dealuminization all three lattice parameters change about equally, and it is postulated that this region represents aluminum removal from the 1 position. Supporting this assertion are the equal projections of the 1 tetrahedra onto *a*, *b*, and *c* and retention of crystallinity. Integrity of the mordenite structure in the *a* direction is maintained only by the four-membered rings comprising 3 and 4. These positions would be then the most tenaciously held and their elimination would be the most destructive to the zeolite.

Each of these three basic sites contains 16 tetrahedra or a third of the unit cell of 48. On the basis of the trends in *a*, *b*, and *c*, one would distribute the 8 aluminum atoms/uc into an average of 2 in position 2, 4 in position 1, and 2 in positions 3 and 4. Such a distribution would explain both the stability of the mordenite structure toward mild dealuminization (removal of isolated tetrahedra from a secondary building unit) and the instability of mordenite toward very strong acid (nonselective aluminum removal, from the 3 and 4 positions). It would also account for the limiting behavior noted in several dealuminization experiments, a behavior of itself suggesting different types of aluminum siting. A more detailed siting is not possible on the basis of these data but aluminum ordering within these three basic locations is certainly not excluded.

No speculation has been made regarding the fate of the structural defects left by aluminum removal. In Y-type zeolites, prepared by EDTA extraction, it appears probable that such defects are filled by silicon (silicate?) migration.[14] Under present conditions of strong acid, low temperature, and brief treatment times, it is difficult to imagine such a process. Furthermore, the excellent agreement of ammonia desorption data and elemental analysis militates against any appreciable silica contaminants. For these reasons the formation of new Si–O–Si bonds suggested by Barrer and Klinowski is presently accepted.[15]

Conclusions

The changes in lattice parameters were determined from x-ray diffraction data for dealuminized mordenites of SiO_2/Al_2O_3 = 10–100. Plots of *a*, *b*, and *c* dimensions vs. Al/uc were strongly nonlinear and suggested, on the basis of a structural projection in the three respective directions, that the aluminum atoms are distributed in three basic types of siting within the mordenite framework. About one-fourth are assigned to position 2 and are readily removed by acid. Half are in 1, and the remaining fourth are in 3 and 4, the 3 and 4 types being removed only with difficulty and often with accompanying structural collapse.

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Registry No. Mordenite, 12173-98-7.

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