THE PREPARATION OF ULTRA-HIGH SILICON FAUJASITES
BY CONTROLLED-RATE ALUMINIUM REMOVAL

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A new technique is described which effects removal of up to 80% of the tetracoordinate aluminium from zeolite Y with retention of 60 to 70% of the crystallinity. Some of the chemical and physical properties of very high SiO_2/Al_2O_3 ratio samples have shed new light on fundamental aspects of faujasite crystal chemistry. These findings should have catalytic significance.

Introduction

It is now well-established that removal of up to about one-half of the tetrahedrally coordinated aluminium significantly increases the thermal and hydrothermal stability of zeolite Y [1—4]. A review of several methods for effecting aluminium removal was recently published [5]. One method which has received wide attention from workers in catalytic studies of zeolites [6] involves the reaction of sodium or ammonium zeolite Y with ethylenediaminetetraacetic acid (H_4EDTA) [2, 3]:
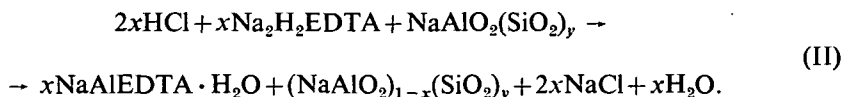
$$xH_4EDTA + NaAlO_2(SiO_2)_y \rightarrow xNaAlEDTA \cdot H_2O + (NaAlO_2)_{1-x}(SiO_2)_y + xH_2O \quad (I)$$

This reaction is conducted in a Soxhlet extractor: the zeolite, slurried in water, is contained in the boiling flask and the H_4EDTA is contained in the Soxhlet thimble. In this way a dilute solution of the acid is added over a 16 to 24 hour period to the zeolite. Attempts to remove more than 50 or 60% of the aluminium *via* this method results in severe losses in crystallinity and thermal stability. The work presented here describes a method for removing 80% of the aluminium with retention of 60 to 70% of the crystallinity. The results of this study shed significant light on some basic aspects of the crystal chemistry of aluminium-deficient faujasites.

Experimental

The new technique consists of carefully controlling the rate of addition of hydrochloric acid to a slurry of the zeolite in a solution of the appropriate di-metal cation dihydrogen ethylenediaminetetraacetate. For example, with the ammonium zeolite, $(NH_4)_2H_2EDTA$ is used; for the sodium zeolite, the acid salt Na_2H_2EDTA

is used. The rate of addition of HCl solution must be such that 10% of the tetrahedral aluminium is removed per day. The overall theoretical stoichiometry of the reaction is:

$$2x\text{HCl} + x\text{Na}_2\text{H}_2\text{EDTA} + \text{NaAlO}_2(\text{SiO}_2)_y \rightarrow$$

(II)

$$\rightarrow x\text{NaAlEDTA} \cdot \text{H}_2\text{O} + (\text{NaAlO}_2)_{1-x}(\text{SiO}_2)_y + 2x\text{NaCl} + x\text{H}_2\text{O}.$$

The reaction products differ from those of reaction I in that sodium chloride is formed in addition to the other products. Thus, the effect of the hydrochloric acid is diminished as the reaction proceeds since the hydronium ion now competes with additional sodium ion, i. e., in addition to sodium ion derived from the sodium zeolite, sodium ion from $\text{Na}_2\text{H}_2\text{EDTA}$ is present in solution.

A typical aluminium removal using this new procedure is described in detail. The ammonium zeolite Y contained 7.47% NH_3 and consisted of 71.4% ash. To exchange one-third of the ammonium ion according to reaction II (and thus at least one-third of the aluminium) from 50.0 g of the ammonium zeolite

$$50 \cdot 0.714 \cdot 0.0747 \cdot \frac{0.333}{17.03} = 0.0518 \text{ moles or } 51.8 \text{ mmoles EDTA}^{4-} \text{ is required.}$$

The 50 g of zeolite was slurried with 51.8 ml of 1 M $(\text{NH}_4)_2\text{H}_2$ EDTA solution (51.8 mmoles) and 300 ml of water. The mixture was stirred and refluxed while 33.3 ml of 3.14 N hydrochloric acid solution (105 mmoles) was pumped continuously into the zeolite slurry over a period of 3.3 days. The zeolite was then collected on a Büchner funnel and washed with one liter of water. The above treatment was conducted two more times. These three batch treatments were considered necessary to reduce the effect of "excess" ammonium ion in solution which might interfere with the necessary exchange of hydronium ion for ammonium ion in the zeolite. The addition of a total of 100 ml of the hydrochloric acid solution would effect 100% removal of NH_4^+ and Al if reaction II were rigorously obeyed. Small aliquot portions of the reaction mixture were removed at the conclusion of the first treatment and during the last two HCl additions and complete elemental and X-ray diffraction analyses were performed on the zeolite samples.

Results and Discussion

Table I presents a resumé of the experimental results and Figs. 1 and 2 graphically present the most important results. In Fig. 1 the unit cell length, a_0, and the percent crystallinity are plotted as a function of the number of aluminium ions per unit cell (Al/U. C.). Two straight lines are shown for the a_0 vs. Al/U. C. plot. A mathematical analysis of the data by W. P. BURGESS at the time of his association with this laboratory showed that two straight lines give a better overall fit of the data than does one straight line involving all ten data points. These two lines each have a terminus in the region of 32 Al/U. C. which corresponds to exactly 2 Al and 10 Si per hexagonal prism or 5.00 Si/Al ratio. This observation appears to be highly significant when compared with the results of DEMPSEY, KUHL and OLSON [7]. They showed that a plot of a_0 vs. Al/U. C. for a variety of synthetic faujasites with Si/Al ranging from 1.00 to about 3.0 best fit three straight lines. One line covers the range correspond-

Table I

ml. HCl added	Wt. % SiO$_2$	Wt.% Al$_2$O$_3$	$\frac{SiO_2}{Al_2O_3}$	% Al remo-ved	Al/U. C.	$\frac{NH_4^+}{Al}$	%. cryst.	a_0, A
0	74.2	24.6	5.13	0	54	0.91	100	24.795
33.3	78.7	20.0	6.7	24	44	0.80	93	24.654
43.3	76.1	16.9	7.7	33	39.5	0.88	87	24.612
53.3	79.1	15.4	8.7	41	36	0.84	83	24.543
63.3	82.8	13.1	10.8	53	30	0.88	82	24.503
66.6	85.4	12.5	11.7	56	28	0.83	82	24.476
76.6	86.7	11.6	12.7	60	26	0.82	76	24.470
86.6	85.5	9.8	14.9	66	22	0.78	69	24.403
96.6	91.8	7.9	19.7	74	17	0.60	67	24.361
100.0	91.3	6.2	25.2	80	14	0.62^a	67	24.335

a — On treatment with NH$_4$OH, NH$_4^+$/Al=0.98.

ing to 6 Si and 6 Al (Si/Al=1.0) and 5 Al and 7 Si per hexagonal prism (1.4 Si/Al). Another line ranges up to 4 Al and 8 Si per prism (Si/Al=3.0). These three lines are displaced in the direction of higher a_0 values as the Al/U. C. range is decreased. Figure 1 shows this same displacement. That the discontinuity in the a_0 *vs.* Al/U. C. data is real is supported by other aspects of our results. Crystallinity *vs.* Al/U. C. follows a straight line from 54 Al/U. C. (the zeolite Y starting material) to about 35 Al/U. C. Then the crystallinity remains constant upon further aluminium removal until 26 to 28 Al/U. C. remain in tetrahedral sites. Upon removing still more aluminium to
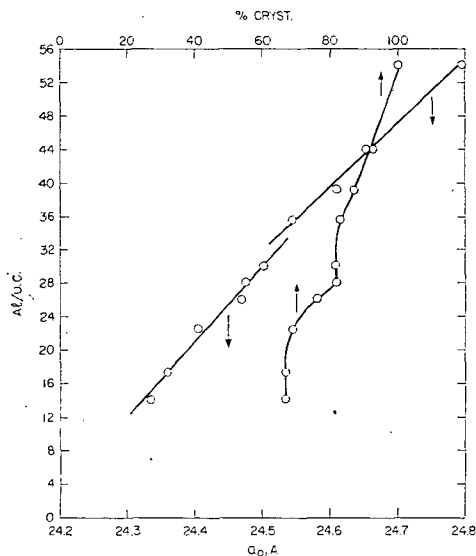

Figure 1. Percent Crystallinity and Unit Cell Parameter *vs.* Aluminium Atoms Per Unit Cell
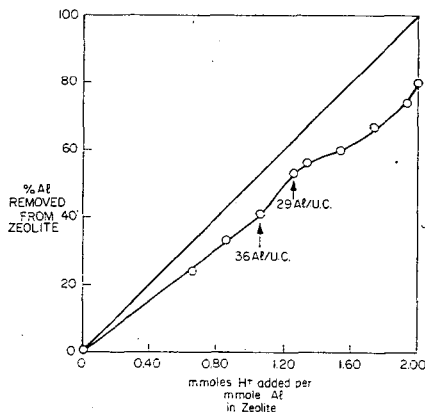

Figure 2. Stoichiometry of Aluminium Removal

the 18 to 20/U. C. level the crystallinity again decreases. The important point is that there is a pronounced inflection in the crystallinity *vs.* Al/U. C. curve in the region of 32 Al/U. C. or one aluminium per six ring.

In Fig. 2, showing the observed stoichiometry compared with that dictated by reaction II (the straight line), an inflection again is apparent in the 32 Al/U. C. region. Indeed, the experimental results indicate that aluminium removal is enhanced in the 36 to 29 Al/U. C. region and then additional aluminium removal becomes more difficult. Note that the final product (80% Al removal) contained only 0.62 NH_4^+/Al but on treatment with NH_4OH this value increased to 0.98 indicating that 40% of the cation sites in the final product are hydrogen or hydronium ion and the four coordinate aluminiums associated with these cations resist hydrolysis and framework removal.

The deviation of the experimental points from the straight line in Fig. 2 over the whole range of aluminium removal is in sharp contrast with the results using the procedure of reaction I where the stoichiometry is very closely followed [2]. The deviation of the experimental points from the stoichiometry of reaction II is attributed in part to the additional ammonium ion in the aqueous phase which depresses hydronium ion exchange into the ammonium zeolite.

The crystallinity data shown in Fig. 1 imply that a portion of the crystalline component becomes amorphous and serves as a source of silica. This raises the questions: (1) what is the composition of the amorphous component? and (2) why isn't all of the available Si used leaving either a very Al rich amorphous phase or no amorphous phase whatsoever?
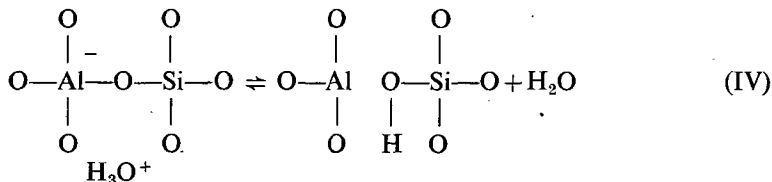
Although the composition of the amorphous phase is not know, it is unlikely to be more Al rich that the crystalline phase. It is also possible that Al in portions of the amorphous phase retaining the short range order of the crystalline phase may possess the same resistance to acid attack as Al in the crystalline phase. In view of the lack of any definitive data concerning this questions, we have assumed the two phases to have identical compositions.

The vertical portions of the Al/U. C. *vs.* % crystalline curve of Fig. 1 imply that the Si replacing the removed Al is being supplied solely by the existing amorphous phase in the ranges 28 to 36 and 14—22 Al/U. C. That the Si of the amorphous phase is not completely consumed indicates that some silica fragments are more reactive than others. One would expect that the reactivity of Si would decrease as the number of Si—O—Si linkages increase, *i. e.*, the Si in a 4-ring of Si tetrahedra may be very resistant to Si transport to the crystalline phase.

Further discussion of the significance of 32 Al/U. C. is warranted. In a series of papers, BEAUMONT and BARTHOMEUF [8—10] showed that about 30 Al/U. C. in a hydrogen zeolite Y contribute strongly acidic sites and that sites associated with more than about 30 Al/U. C. are moderately to weakly acidic. They observed that aluminium removal from zeolite Y, to about the 30 Al/U. C. level using the H_4EDTA method, resulted in a loss in total acidity but no loss in strongly acidic sites. From this observation they drew the logical conclusion that weakly acidic sites and the associated framework aluminiums are preferentially removed by the H_4EDTA method. This is to be expected using the argument that upon treatment of a sodium or ammonium Y with H_4EDTA-water slurries, H_3O^+ is exchanged into the zeolite:

$$NaY + H_3O^+ \rightarrow H_3OY + Na^+ \hspace{3cm} \text{(III)}$$
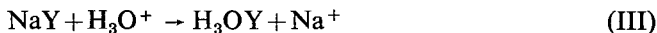
An equilibrium is established between the hydronium form of the zeolite and the hydrogen form:

$$
\begin{array}{cccc}
O & O & O & O \\
| - & | & | & | \\
O-Al-O-Si-O & \rightleftharpoons & O-Al & O-Si-O+H_2O \\
| & | & | & | \quad | \\
O & O & O & H \quad O \\
H_3O^+ & & &
\end{array}
\qquad (IV)
$$

Obviously the equilibrium would lie to the right of reaction IV for weakly acidic sites and to the left for strongly acidic sites. KERR proposed that aluminium removal involves the hydrolysis of aluminium from the hydrogen zeolite in which disruption of an Al—O bond occurred [2]. Therefore, one would expect the weakly acidic sites to undergo aluminium removal in preference to strongly acidic sites. Also of significance is the observation of BEAUMONT and BARTHOMEUF that deepbed calcined NH_4Y or ultrastable Y contains about 30 Al/U. C. or that about one-third of the aluminium in the initial NH_4Y of HY undergoes transition from four to six coordinate aluminiums. Again, it is the weakly acidic sites which are lost while strongly acidic sites are retained.

As observed previously [2], the thermal stability of zeolite Y increases as the Si/Al ratio increases. The final sample prepared in this series ($SiO_2/Al_2O_3 = 25.2$ or 80% aluminium removal) underwent lattice collapse at 1260° using a DTA test for thermal stability [11]. Hitherto, the two most stable faujasites observed by this test were stable hydrogen zeolite Y (1058°) and rare earth zeolite Y (1040°). A sample of the 25.1 SiO_2/Al_2O_3 zeolite was treated with 3 N HCl solution at reflux for 18 hours to yield a 46% crystalline material ($a_0 = 24.259$ A) which was still crystalline after heating to 1272°, the upper limit of our DTA furnace. This sample contained 99% SiO_2 and 1 to 2% Al_2O_3 or a molar ratio SiO_2/Al_2O_3 of at least 50 and perhaps as high as several hundred.

Unquestionably, the most important aspect of the new technique is the rate of addition of hydronium ion and thus, very likely, the rate of removal of aluminum. If it is assumed that silicon atoms or ions migrate into sites vacated by aluminum, as suggested by several workers [12, 13], it is reasonable to assume that this is a slow process at 100°. Thus, if the removal of aluminum proceeds at a faster rate than the migration of silicon into defect sites, then a catastrophic defect situation arises and the crystal structure collapses. Should the exchange of hydronium ion into the zeolite (and thus removal of framework aluminum) proceed at a rate equal to or somewhat less than the rate of silicon migration, then the zeolite can "heal" itself and retain most of the crystallinity even up to quite high levels of aluminum removal. There is nothing unique about the mechanics described in this new technique. It is only a simple and convenient way of carefully controlling the rate of hydronium ion exchange into the zeolite. Indeed, the initial observation that 80% aluminum removal could be effected with retention of most of the crystallinity involved the use of the Soxhlet extractor method with H_4EDTA. In this case, however, a considerably larger scale reaction was conducted than in the past and ten days were required to dissolve and introduce the H_4EDTA into the zeolite slurry rather than the usual 18 to 24 hours. This observation led, ultimately, to the development of the new procedure which involves the removal of 10% of the aluminum per day. When the

new technique was used over a 13.5 day span, the same degree of aluminum removal was achieved but the crystallinity of the final product was about 50%, indicating that the 10% removal per day is critical.

These results suggest that KERR's proposal [3] that aluminum is first replaced by three protons and that upon heating, water is driven from these sites to form new (and somewhat distorted) Si—O—Si bonds is wrong. The first step is reasonable; the second step probably involves the replacement of four protons (total charge $+4$) by a silicon ion, Si^{+4}.

Acknowledgment

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