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Structural Stability of Partially Ammonium-Exchanged Zeolite A

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The thermal stability of the crystal structure of NaHA increases rapidly when the ratio of Na/Al rises above 0.33. The least damage to the structure occurs at a slow heating rate in a dry atmosphere. The hydrothermal stability of NaHA increases at a ratio of Na/Al in the range of 0.5 to 0.7. Both stabilities depend on the number of cation equivalents per unit cell, not on the number of cations. Zeolite A that is partially in the hydrogen form and thermally stable, can tolerate the sorption of small amounts of water and recalcination without losing crystallinity.

INTRODUCTION

All attempts to prepare a pure 100% hydrogen zeolite A have failed. The methods tried included the following:

Slow calcination of ammonium zeolite A to remove the water before the decomposition of the ammonium ion starts (*1*). Slow calcination of NH_4A in a stream of ammonia. Dehydration of NaA at 500°C in flowing nitrogen and subsequent reaction with dry hydrogen chloride. All of these experiments yielded amorphous products.

We found then that a partially ammonium-exchanged zeolite A remained crystalline upon calcination if the degree of exchange was not more than 50%. Recalcination after water sorption caused a breakdown of the crystal structure.

These observations initiated a more detailed investigation, the results of which are reported in this paper.

METHODS

1. Preparation of Sodium Ammonium Zeolite A

The exchange of sodium zeolite A (Linde Co., Lot No. 47077, 41.2% SiO_2, 35.6% Al_2O_3, 21.65% Na_2O) with ammonium chloride at ambient temperature is shown in Fig. 1. The curves for the increasing ammonium and decreasing sodium content are approximately symmetrical about a cation/Al atomic ratio of 0.46. The total cation/Al ratio of the zeolite averages about 0.92. This means that about 8% of the sodium ions—corresponding to 1 ion/unit cell or per sodalite cage—are exchanged with hydronium rather than with ammonium ions. These hydrogen sites permit hydrolysis of framework-aluminum, but a significant degree of hydrolysis may not occur at ambient temperature. Hydronium ion exchange is a problem that we have not been able to eliminate by neutralizing the ammonium chloride, nitrate or sulfate solution with ammonium hydroxide.

The composition of the ammonium-exchanged samples is given in Table 1.

2. Preparation of Calcium Ammonium Zeolite A

Ammonium zeolite A ($NH_4^+/Al = 0.89$; $Na^+/Al = 0.03$) was exchanged with 0.2 N $Ca(NO_3)_2$ solution at ambient temperature (Fig. 2). The (equiv $Ca^{2+} + NH_4^+$)/Al ratio remained at 0.89; any deviations are presumably caused by the accumulation of

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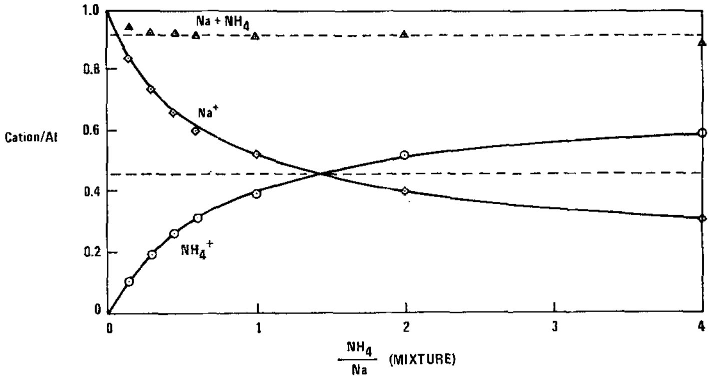

FIG. 1. Exchange of sodium zeolite A with ammonium chloride.

TABLE 1
COMPOSITION OF $NaNH_4A$ SAMPLES

Sample no.	NH_4^+/Na	Product NH_4^+/Al	Product Na^+/Al	Product H_3O^+/Al
1	0.15	0.105	0.844	0.051
2	0.3	0.191	0.739	0.070
3	0.45	0.264	0.665	0.071
4	0.6	0.312	0.601	0.087
5	1.0	0.390	0.523	0.087
6	2.0	0.519	0.400	0.081
7	4.0	0.590	0.299	0.111

small analytical errors in the individual determinations.

The isotherm for the exchange of ammonium zeolite A ($NH_4^+/Al = 0.86$; $Na^+/Al = 0.03$) with 0.2 N calcium acetate solution is shown in Fig. 3. Hydronium ions introduced during the ammonium exchange were not removed by treating the zeolite with 0.2 or 2 N calcium acetate solution.

When a sample of NH_4A was dried at 110°C, some ammonia was lost; the ratio NH_4^+/Al was only 0.78 after this treatment. Upon calcium exchange with 0.2 N $Ca(NO_3)_2$ the ratio equiv Ca^{2+}/Al increased only to about 0.3, while the ratio NH_4^+/Al did not fall below about 0.47. This large number of ammonium ions was unexchangeable. The X-ray diffraction pattern and the n-hexane sorption capacity indicate that the product was only about 30% crystalline corresponding to the degree of calcium exchange. The nonexchangeable NH_4^+ ions are, therefore, located in the amorphous part of the sample.

3. *Determination of the Stability of Zeolite A*

The thermal stability of a zeolite A type material can most easily be judged by the

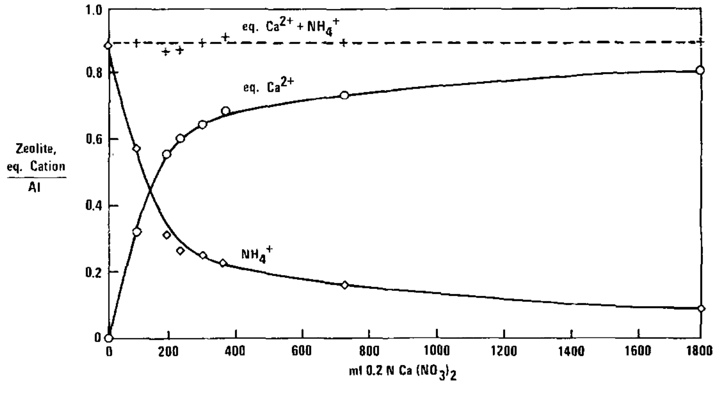

FIG. 2. Exchange of ammonium zeolite A with calcium nitrate. 10 g of NH_4A (67% ash).

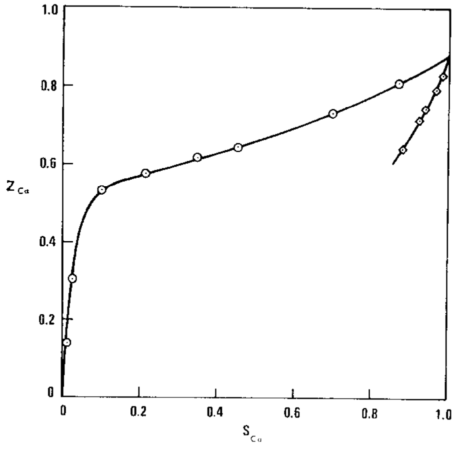

FIG. 3. Exchange isotherm of ammonium zeolite A with calcium acetate at 25°C. (○) 0.2 *N*; (◇) 2 *N*.

n-hexane sorption capacity of the zeolite. It has to be remembered, though, that the zeolite must not contain more than 10 cations/unit cell, i.e., at a Na/Al atom ratio above about 0.833 the structure cannot sorb *n*-hexane because less than two 8-ring windows/unit cell remain open.

A DuPont Model 950 thermogravimetric analyzer was used for calcination at various heating rates, with dry helium flowing through the sample chamber at a flow-rate of 175 ml/min. At 550°C constant weight was attained, and the sample was allowed to cool to room temperature. Helium, loaded with the sorbate, was then passed through the sample chamber and the weight increase caused by sorption was measured at atmospheric pressure. When a sample had been calcined in a moist atmosphere, the excess water was removed by passing dry helium over the sample for at least 10 min before cooling.

Since the unit cell weight of the calcined zeolite changed with degree of exchange, the sorption capacities were calculated as moles of sorbate per mole of SiO_2 in the sample.

The crystallinity of a number of samples was estimated from the Debye-Scherrer patterns. The results were in good agreement with those obtained from the *n*-hexane sorption data.

RESULTS

The pure hydrogen form of zeolite A is not stable because too many Al–O bonds are broken upon hydrogen ion attack on the aluminosilicate framework. One out of four bonds of every other tetrahedron is affected; it can easily be shown on a model that the zeolite A structure breaks down when such a reaction occurs.

Preliminary Experiments

We had found previously that only those samples of zeolite A that were exchanged to more than 50% with ammonium ions were thermally unstable. The hydrothermal stability of the NaHA obtained by calcination of the samples exchanged with ammonium to a lesser degree, decreased with increasing degree of exchange.

In an effort to control the hydrolysis of framework-aluminum and to show the effect of water on the crystallinity during calcination, products 1, 2, 4, and 5 (Table 1) were calcined in two different ways, in a thin layer and in a thick layer, corresponding to shallow bed and deep bed calcinations, as described by Kerr (*2*). The crystallinity was determined from the water sorption capacity, and the hydrothermal stability of the product by repeated water sorption at 12 mm and 25°C (*3*). The results are shown in Tables 2 and 3.

The two different calcination methods gave similar results for samples 1 and 2, although it is evident that the loss of crystallinity from the first to the third calcination of sample 2 was greater from the thin layer calcination. This trend was

TABLE 2

CALCINATION IN A THIN LAYER AT 550°C

	Water sorption capacity (g/100 g of zeolite) after		
Sample no.	1st calcination	2nd calcination	3rd calcination
1	26.7	26.1	25.1
2	27.8	25.0	23.1
4	28.0	16.0	11.8
5	23.0	3.5	1.0

TABLE 3

Calcination in a Thick Layer at 550°C

Sample no.	Water sorption capacity (g/100 g of zeolite) after		
	1st calcination	2nd calcination	3rd calcination
1	26.6	26.2	25.6
2	26.8	25.2	24.9
4	26.0	21.6	18.2
5	14.9	6.0	3.4

considerably enhanced in sample 4. The water sorption capacity after deep bed calcination was 26 g/100 g of zeolite compared to 28 g/100 g of zeolite after thin layer calcination. The loss of crystallinity from the first to the third sorption, however, was considerably smaller after the deep bed calcination. The final water sorption capacity was still about 70% of the original value whereas the sample initially calcined in a thin layer retained only about 40% of its original crystallinity.

The n-hexane sorption capacity (at 20 mm and 25°C) (*3*) was higher after the thin layer calcination (Table 4), but never reached the regular value for the zeolite A structure (12.6 g of n-hexane/100 g of zeolite 5A). Since the water sorption capacity after the shallow bed calcination was normal, we suspected that hydrolysis of framework-aluminum occurred to some degree resulting in partial obstruction of the zeolite pores to n-hexane. In order to minimize this hydrolysis, all subsequent calcinations were carried out with small, about 50 mg, samples in the TGA unit.

TABLE 4

n-Hexane Sorption Capacity

Sample no.	n-Hexane sorption (g/100 g of zeolite) after	
	Thin layer calcination	Thick layer calcination
1	0.51	0.40
2	0.75	0.79
4	5.95	1.43
5	3.07	0.71

Thermogravimetric Results

Sodium ammonium zeolite A samples were calcined in flowing dry helium at a heating rate of 20°C/min. After reaching constant weight at 550°C and cooling to ambient temperature, n-hexane was sorbed (Fig. 4). At low Na/Al ratios, no sorption was observed. A check by X-ray diffraction proved that the calcination product was amorphous. At medium sodium content, high n-hexane sorption capacities were found. The sample with Na/Al = 0.739 had a n-hexane sorption capacity of only 0.9 g/100 g of zeolite. Heating rates of 10 and 5°C/min caused the product to have higher sorption capacities. The n-hexane sorption of this sample 2 was quite slow regardless of calcination conditions. Sample 6, Na/Al = 0.400, had also a significantly higher n-hexane sorption capacity after calcination at a rate of 5°C/min than after having been calcined at 20°C/min heating rate.

n-Hexane can be adsorbed and desorbed reversibly without loss of crystallinity. Even the sorption of small amounts of water does not cause a loss in sorption capacity, when the zeolite is recalcined:

Sample 5, Na/Al = 0.523	
n-Hexane sorption, g/100 g of zeolite	13.5

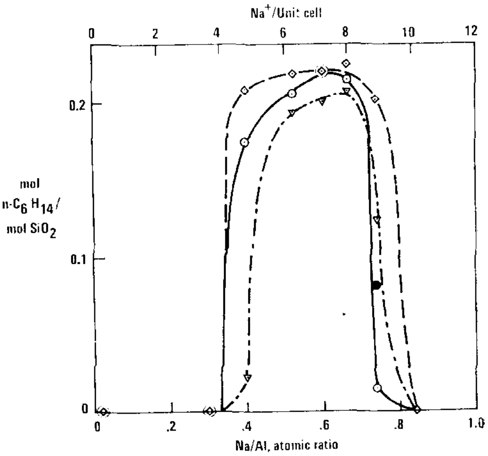

Fig. 4. Structural stability of $NaNH_4A$ upon calcination. (◇) 5°C/min, dry He; (●) 10°C/min, dry He; (○) 20°C/min, dry He; (▽) 30°C/min, moist He.

Recalcined, n-hexane sorption, g/100 g of zeolite	13.5
Recalcined, amount of H_2O sorbed, g/100 g	6.0 (not saturated)
Additional n-hexane sorption, g/100 g	7.5 (saturated)
Recalcined, n-hexane sorption, g/100 g	13.2

The results indicate essentially complete retention of structure.

When $NaNH_4A$ samples were calcined at 30°C/min in water-loaded helium atmosphere (Fig. 4), sample 6, Na/Al = 0.400, gave a low, sample 2, Na/Al = 0.739, a relatively high n-hexane sorption capacity.

Figure 5 shows the water sorption after calcination at different heating rates. In order to compound the effect of the fast rate, the flowing helium was saturated with water vapor. The sorption capacities of the slowly heated samples were always slightly higher, but generally the values do not differ significantly.

A zeolite sample calcined at 30°C/min is not necessarily hydrothermally stable. After the first, relatively high water sorption (Fig. 5), the samples were recalcined at 30°C/min to 550°C. The products sorbed no or very little n-hexane. The results of the second water sorption are also shown in Fig. 5. The degree of crystallinity can be estimated from this water sorption. The X-ray diffraction pattern was stronger and sharper the higher the water sorption. In general, the zeolites initially calcined at 30°C/min in a moist atmosphere gave products that were somewhat more hydrothermally stable than those obtained by initial calcination at 5°C/min in dry helium.

The structural stability of $CaNH_4A$ to calcination is shown in Fig. 6. No great differences were found for the different calcination conditions. The results are very similar to those obtained with $NaNH_4A$, except that the n-hexane sorption did not drop to zero at equiv Ca/Al of about 0.85. The hydrothermal stability of CaHA was determined by measuring the n-hexane sorption capacity after water sorption and recalcination (Fig. 6). The zeolite A structure appears to be completely stable at a ratio equiv Ca/Al of 0.8 or higher. A very slight advantage was observed when the zeolite was calcined fast in a moist atmosphere. The curves for the water sorption are similar (Fig. 7) to those for the n-hexane sorption.

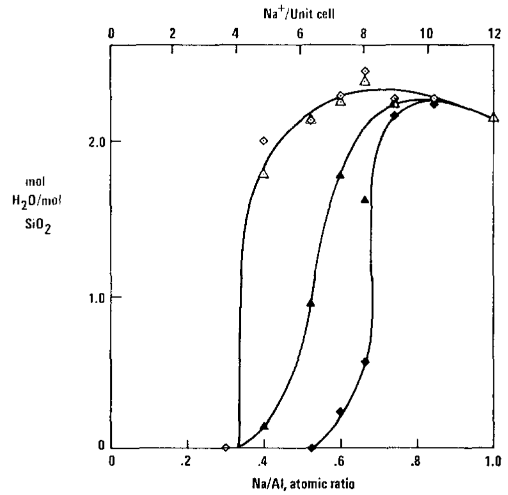

FIG. 5. Structural stability of $NaNH_4A$ upon calcination and hydrothermal stability of NaHA. (◇) 5°C/min, dry He; (△) 30°C/min, moist He; (◆▲) after recalcination at 30°C/min.

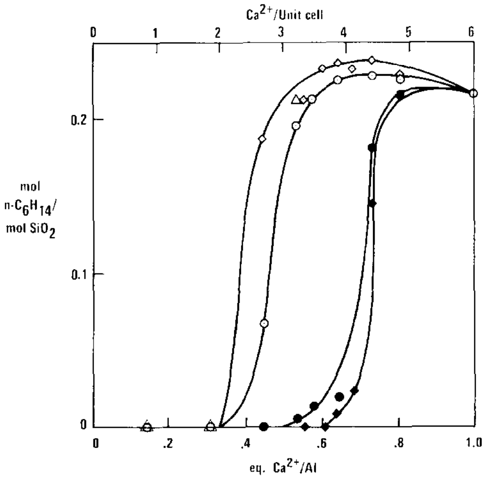

FIG. 6. Structural stability of $CaNH_4A$ to thermal and hydrothermal treatment. (△) 5°C/min, dry He; (◇) 10°C/min, dry He; (○) 30°C/min, moist He; (◆●) after water sorption and recalcination at 30°C/min.

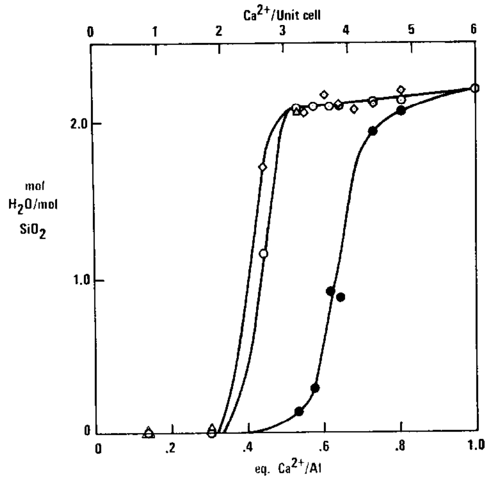

FIG. 7. Structural stability of $CaNH_4A$ to thermal and hydrothermal treatment. (△) 5°C/min, dry He; (◇) 10°C/min, dry He; (○) 30°/min, moist He; (●) after water sorption and recalcination at 30°C/min.

Cracking Activity

The *n*-hexane cracking activity of calcium hydrogen zeolite A, although low compared with the hydrogen forms of high-silica zeolites, is higher than that of calcium zeolite A (Table 5).

DISCUSSION

The reactions occurring upon calcination of ammonium zeolites in the absence or in the presence of water are generally the same for all zeolites. Differences in structural stability are, however, observed, depending on the particular zeolite structure and the SiO_2/Al_2O_3 ratio.

TABLE 5
n-HEXANE CRACKING ACTIVITY (*11*) OF CALCIUM HYDROGEN ZEOLITE A

Equiv Ca/Al	α-values after 5 min	18 min	30 min	Regeneration
0.579	2.9	1.0	—	0.7
0.732	0.9	1.0	—	1.1
0.899	0.5	—	0.4	0.7

Most previous work has been done on zeolite Y. Calcination of an ammonium zeolite under anhydrous conditions yields a true hydrogen zeolite (*4–6*). If a sufficient concentration of water is present during the calcination, a material containing cationic aluminum and defects in the zeolite framework is formed (*2*, *7*). These aluminum cations prevent further hydrolysis of aluminum from the framework and thus stabilize the zeolite structure. When water is sorbed on a true hydrogen zeolite, a hydronium zeolite is formed. This reaction cannot be reversed by calcination; instead, massive hydrolysis of framework-Al occurs, and the crystal structure collapses (*2*).

The 5°C/min calcination in a dry helium stream (Fig. 4) approaches closely the formation of a true sodium hydrogen zeolite A. The results show that the material requires at least 4 sodium ions/unit cell for structural stability. With about 9 Na^+/unit cell, the *n*-hexane sorption begins to decrease. After calcination at heating rates of 10 and 20°C/min in a dry helium stream, the *n*-hexane sorption capacities for this sample are successively lower. Since 10 cations/unit cell are required to block the pores for *n*-hexane (*8*, *9*), this observation can be explained only by hydrolysis of framework-aluminum and increase of the number of cations by formation of cationic aluminum. The slow sorption of *n*-hexane on this material is further indication that additional cations have been formed (*10*).

After calcination at 30°C/min in a moist atmosphere, the sorption capacity for *n*-hexane was higher than after 10 and 20°C/min calcination in dry helium. A high water concentration permits the cations to be more mobile so that the hydroxylated aluminum cations can be neutralized to a greater degree than in the presence of only small amounts of water. In this way, the aluminum cations, by neutralizing a greater number of acid sites, acquire a higher charge, so that the number of aluminum cations formed is actually smaller than in the samples hydrolyzed with an insufficient amount of water. A true hydrogen zeolite, of course, contains no cationic aluminum and has, therefore, always fewer cations than the same sample calcined with an excess of water.

At 0.4 Na/Al, on the other hand, the loss of crystal structure increases with rising concentration of water during the calcination. With 4 sodium ions/unit cell, the structure collapses even if the material is calcined in a water-free atmosphere. With slightly more sodium present (4.8 Na^+/unit cell), the least additional damage by hydrolytic reaction causes also collapse of the zeolite structure.

When the zeolite samples were recalcined after water sorption, they sorbed practically no *n*-hexane. The reason can be collapse of the structure or blockage of pores. The structural stability after this treatment (hydrothermal stability), therefore, had to be checked by water sorption. Figure 5 shows a considerable difference in this hydrothermal stability depending on the conditions of the initial calcination. Sorption of water on a true NaHA (5°C/min) and recalcination caused massive hydrolysis and loss of crystal structure, whereas the zeolite calcined initially in the presence of water retained the structure much better because of stabilization by aluminum cations. Complete stability was attained with 10 Na^+ ions/unit cell or more.

Because of the fewer cations, the hydrothermal stability of CaHA could be determined by sorbing *n*-hexane (Fig. 6). Perfect stability was found only with 10 or more equivalents of Ca^{2+}/unit cell. This result is corroborated by the data obtained from the water sorption.

Comparison of the stability experiments of NaHA and CaHA indicates that the stability depends on the ratio cation equivalents/Al, or, expressed in a different way, the number of AlO_4 tetrahedra per unit cell associated with stable cations, not on the number of stable cations per unit cell.

A zeolite that is at least partially in the hydrogen form, is expected to catalyze cracking of hydrocarbons, provided the pores are sufficiently large to enable the hydrocarbon to enter. The zeolite A structure is of particular interest because the 5 Å pore apertures admit straight-chain hydrocarbons, but not branched-chain and cyclic hydrocarbons, thus allowing shape-selective cracking.

The *n*-hexane cracking activities of a number of zeolites were measured by Miale, Chen and Weisz (*11*). Zeolites that were, at least partially, in the hydrogen form after calcination were found to possess high activities for cracking *n*-hexane. The activity of the pure calcium forms increased with rising SiO_2/Al_2O_3 ratio from calcium zeolite A ($\alpha = 0.6$) over calcium faujasite ($\alpha = 1.1$) to calcium mordenite ($\alpha = 1.8$).

The *n*-hexane cracking activity of a CaHA is expected to be higher than that of CaA. This has been confirmed by our results (Table 5). The initial activity of calcium hydrogen zeolite A appears to be a function of the number of protons per unit cell. The sample with equiv Ca^{2+}/Al = 0.579 reveals its instability by the decrease of the α-value with time and regeneration. The cracking activity of the other two samples increased upon regeneration, thus demonstrating their stabilities. After regeneration, both samples had a higher *n*-hexane cracking activity than calcium zeolite A. The products were primarily olefinic and unbranched as would be expected for a shape-selective catalyst having the pore characteristics of zeolite A.

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REFERENCES

1. KERR, G. T., personal communication.
2. KERR, G. T., *J. Catal.* **15**, 200 (1969).
3. LANDOLT, G. R., *Anal. Chem.* **43**, 613 (1971).
4. SZYMANSKI, H. A., STAMIRES, D. N., AND LYNCH, G. R., *J. Opt. Soc. Amer.* **50**, 1323 (1960).
5. UYTTERHOEVEN, J. B., CHRISTNER, L. G., AND HALL, W. K., *J. Phys. Chem.* **69**, 2117 (1965).

6. Benesi, H. A., *J. Catal.* **8**, 368 (1967).

7. Kerr, G. T., *J. Phys. Chem.* **71**, 4155 (1967).

8. Reed, T. B., and Breck, D. W., *J. Amer. Chem. Soc.* **78**, 5972 (1956).

9. Kerr, G. T., *J. Phys. Chem.* **66**, 2271 (1962).

10. Kühl, G. H., *Inorg. Chem.* **10**, 2488 (1971).

11. Miale, J. N., Chen, N. Y., and Weisz, P. B., *J. Catal.* **6**, 278 (1966).