

Thermal Behavior of Synthetic Faujasite

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Data are presented to show that the thermal stability of synthetic faujasite is dependent on the level of sodium present. A simple relationship has been found between the sodium content of ammonium-exchanged faujasite and the temperature at which breakdown of the zeolite structure occurs. This relationship extends to sodium contents below 0.1%, and demonstrates the existence of a continuum of properties for variously exchanged faujasite samples. Regardless of the degree of sodium removal or the method of exchange employed, X-ray diffraction analysis shows that the faujasite structure is retained to just below the breakdown temperature, that material heated just beyond the breakdown temperature is amorphous, and that material heated further, to beyond the mullitization temperature, contains crystalline mullite. The data obtained support the hypothesis that thermally induced migration of cations is an important part of the mechanism for facilitation of exchange, and for structure degradation as well.

INTRODUCTION

Few precise data are available on the thermal behavior of the synthetic faujasite crystal structure, although semiquantitative and qualitative observations have been made. A change in structure has been claimed to occur with formation of a new phase (1, 2). Some speculations on the nature and mode of formation of catalytically active sites have been advanced (for example, refs. 3 and 4). Cation positions (4-8) and behavior upon decationization (7-12) have also been postulated. In the present work, careful evaluation of X-ray diffraction and high-temperature differential thermal analysis data for variously treated synthetic faujasite samples in the hydrogen form leads to the conclusion that a continuum in properties exists over the range of sodium levels studied.

Normally, synthetic faujasite is prepared in the sodium form, and if other forms are desired, ion exchange of the sodium form is used to prepare them. It is well known that it is relatively easy to remove about two-thirds of the sodium in this way, but further exchange, in general, becomes progressively more difficult as the sodium level decreases.

For example, it is difficult to prepare ammonium-exchanged faujasite with sodium levels of less than about 1% Na₂O by exchange even in boiling hot solutions. However, if one interrupts the exchange at or below the 4% Na₂O level and heats the sample to about 540°C for 2 hr, one can then easily attain Na₂O levels of less than 0.1% by further exchange (1, 2). The resultant material is more thermally stable than ammonium-exchanged faujasites (1-4% Na₂O) prepared in the conventional way.

The question naturally arises as to the reason for the enhanced stability. Is it due to the unusually low sodium level? Or is it perhaps due to some alteration in structure brought about by the unusual treatment (1)?

McDaniel and Maher (M & M) (1) postulate structural differences between conventionally exchanged and "ultrastable" faujasite. These differences are, principally, differences in proton location. Kerr (7, 13) suggests differences resulting from Al migration into vacant cation sites with accompanying charge redistribution. The postulate of M & M seems unlikely in view of the known high proton mobility in these

materials at high temperatures (14). Kerr's postulate appears more attractive, and is further considered below.

In the present work, evidence is presented in support of the hypothesis that the ultra-stable faujasite is not intrinsically different in structure from other ammonium-exchanged faujasites except insofar as it may have a lower sodium level and corresponding unit cell parameter, and therefore, that it constitutes merely a part of a continuous distribution of materials whose relative properties are a function of sodium level (and, possibly, water level), the enhancement of stability being due mainly to the low value of the sodium level.

A quantitative measure of the thermal stability of the various forms of faujasite does not appear to have been adequately described in the literature, although Kerr (13) has taken a step in this direction. The method described herein allows rather precise determination and intercomparison of thermal stability data in terms of the structural breakdown temperature when constant conditions for evaluation are used, affording a more rigorous basis for evaluation than has been heretofore available. The method has been firmly established by our work with ammonium-exchanged faujasites, and has tentatively been found to apply to other cations as well. It is proposed that this method be adopted for the obtention of quantitative data relating to thermal behavior of such materials, using the easily attained heating rate of 25°C/min.

EXPERIMENTAL

Samples of sodium faujasite of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio 4.58 [as determined by X-ray measurements (15)], from an experimental batch obtained from Davison Chemical Co., were partially ammonium-exchanged to various degrees, using two different exchange methods. The first method was a conventional ammonium nitrate (reagent grade) exchange comprising successive treatments with fresh solution, followed by a thorough water-washing schedule. The second method consisted of two successive exchange treatments followed by a 540°C calcination, and then by two further exchanges and thorough

washing. The latter is essentially the procedure of M & M, except that ammonium nitrate was used instead of ammonium sulfate. Several samples of Linde NaY were also used; the results were indistinguishable from those obtained with the Davison material.

DTA scans were made on a du Pont Model 900 Differential Thermal Analyzer adjusted to permit use of maximum ΔT sensitivity (0.12°C/cm) with a dry nitrogen-purged accessory high-temperature cell employing a thermocouple assembly consisting of a matched pair of Pt-Pt, 13% Rh thermocouples. This represents a substantial improvement over conventionally obtained usable sensitivity in the high-temperature region. Sample size was reproducibly packed to about 65 mg, and temperature sensitivity in the region of interest was 24°C/cm. Scanning rate was 25°C/min, controlled by a Platinel control thermocouple. Except for those receiving a final calcination, samples were dried 8 hr at 110°C and tightly bottled before being charged.

X-Ray powder patterns were obtained on a Norelco diffractometer equipped with a pulse-height analyzer and fitted with an MRC hot stage for pretreatment and control of ambient conditions during scanning. Scans were made at 1°/min with nickel-filtered copper $K\alpha$ radiation.

Sodium analyses were performed by conventional flame photometry and gravimetric methods, according to the range encountered (16).

RESULTS AND DISCUSSION

Figure 1 shows DTA scans for four samples of interest. Curves A, B, and C correspond to different degrees of conventional exchange, while curve D represents the intermediate calcination technique of M & M. All partially ammonium-exchanged samples showed essentially similar type patterns in the high-temperature region, differing mainly in the precise temperature of the exotherms. Figure 2 shows a plot of exotherm peak apex temperature vs. sodium oxide content for a series of samples, including some conventionally exchanged and some prepared by the M & M procedure, the

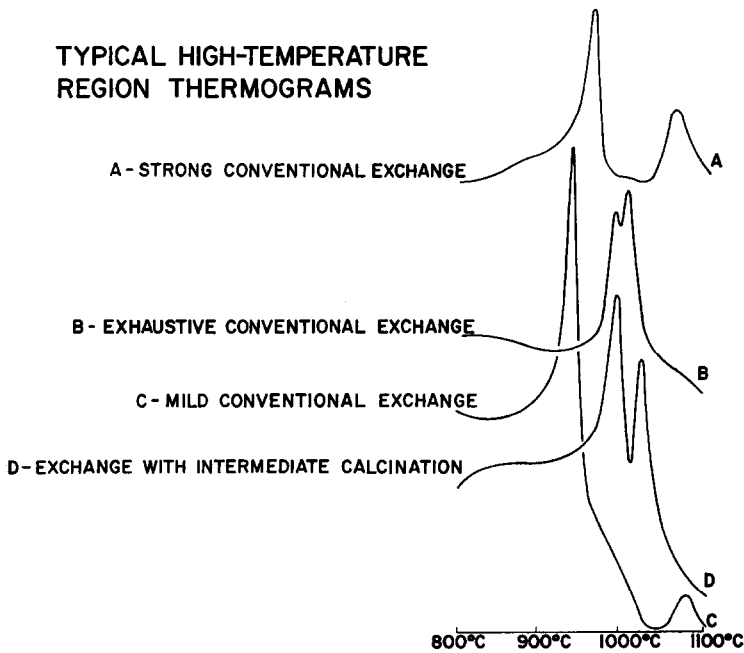


FIG. 1. Typical high-temperature region thermograms; wt. % Na_2O for curve A is 1.20%; for curve B, 0.39%; for curve C, 3.94%; and for curve D, 0.07%.

latter being designated in Fig. 2 as having received an intermediate calcination. The series appears to represent a continuous shift depending only on sodium level, and not perceptibly on method of preparation.

Samples prepared by either exchange method and given a stabilizing calcination, as described by M & M, fall on a curve parallel to that for dried-only samples. The second or mullitization exotherm also appears to shift

EXOTHERM PEAK TEMPERATURES VS. Na_2O CONTENT

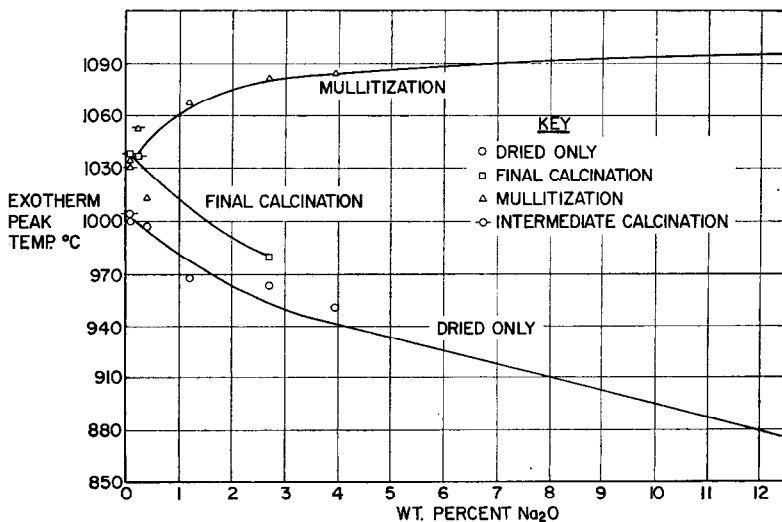


FIG. 2. Exotherm peak temperatures vs. Na_2O content.

monotonically and without discontinuity, with change in the sodium level.

An attempt was made to relate our data to those of Kerr (13) by obtaining a thermogram of NaY run at 30°C/min. The structure collapse temperature obtained was 892°C, in reasonable agreement with the 871°C we found using 25°C/min, and directionally compatible with what would be expected for a kinetically controlled process run at a faster rate of temperature increase. These values do not agree with Kerr's 974°C, in spite of the fact that our pretreatment removed less water from the sample than did his 550–600°C, suggesting that the role of water (?) has been somewhat overemphasized.

It was also found that the intensities of the exotherms observed at comparable sodium levels were approximately equal in the two exchange forms noted above, within the limits of error of DTA intensity measurements. The effect of mechanically admixed diluent on DTA peak position and intensity was examined and found not to be significant. The integrated intensity was directly related to zeolite content in the mechanical mixture, and the peak positions were not significantly different at the 90% confidence level.

The interpretation of the DTA exotherms was investigated by obtaining X-ray diffraction powder patterns of samples prepared in the DTA apparatus by terminating the temperature program at selected temperatures, cooling quickly, and transferring the sample to the X-ray hot stage. Table 1 shows some X-ray data on material from DTA scans terminated at a temperature of 888°C. After calcination in dry N₂ at this temperature, *all* exchanged samples showed a faujasite pattern. Between the two exotherms *all* samples were amorphous. Beyond the second exotherm, mullite was the dominant phase present. Again, there was no qualitative difference observed between "normal" and ultrastable samples.

Lattice constants were also determined from the X-ray data on equivalently treated samples, using standard methods (17, 18). These values, disagreeing with the data of M & M in the region where any change

TABLE 1
LINE INTENSITY DISTRIBUTIONS^a IN THE
X-RAY POWDER DIFFRACTION
PATTERNS OF "ULTRASTABLE"
vs. "NORMAL" FAUJASITES
CALCINED TO 888°C IN
THE DTA APPARATUS

{hkl}	I_u^b (counts/sec)	I_n^b (counts/sec)	Difference
111	104	99	5
220	40	34	6
311	54	42	12
331	80	81	-1
333, 511	50	51	-1
440	66	65	1
620	26	26	0
533	132	135	-3
711, 551	12	12	0
642	94	95	-1
733	30	28	2
822, 660	32	38	-6
555, 751	70	79	-9
840	12	18	-6
664	26	30	-4

^a At 120°C in flowing dry N₂.

^b Peak intensities were used after subtraction of background. I_u was multiplied by a scale factor (close to unity) so that the sum of all lines corresponded with that for the normal material. u, Ultrastable; n, normal.

might be expected to appear (1), proved to be a smooth function of the sodium level, as illustrated in Fig. 3. Again, the method of obtaining a particular sodium level did not appear to make any difference in the measured property, in this case the a_0 value. The unit cell parameters are affected by calcination, exchange treatment, solvation, etc. (19), but should form a family of essentially parallel curves smoothly dependent on sodium level and not on the method employed for sodium removal.

It is of interest to note that the only way that a crystalline phase can transform to an amorphous phase *with evolution of heat* is for the crystalline phase to have become metastable somewhat below the transformation temperature. Such a transition must necessarily be kinetically, rather than thermodynamically, controlled. Yet the transition takes place at roughly the same temperature and with approximately the same heat

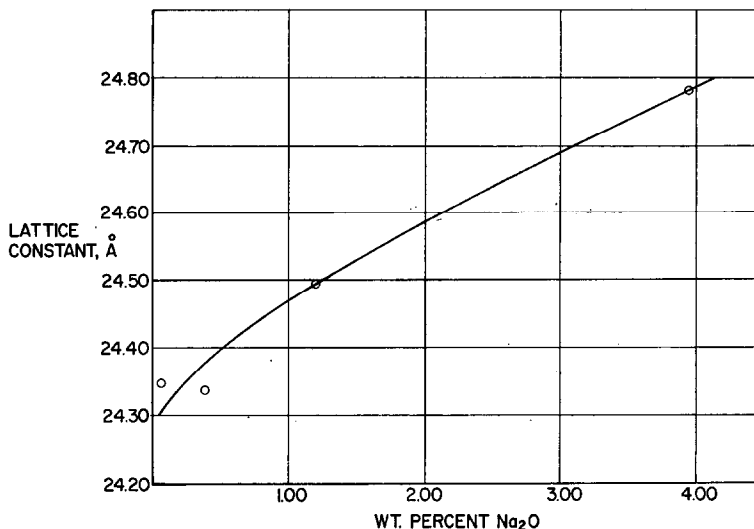
LATTICE CONSTANT VS. Na_2O CONTENT

Fig. 3. Lattice constant vs. Na_2O content. Data were obtained at 120°C in flowing helium, after being held at these conditions overnight.

evolution in the normal and ultrastable samples! Such evidence is diametrically opposed to the "qualitative difference" concept.

Consider, now, the hypothesis that ultrastable and normal forms are structurally different. In what could such a difference consist? That they both belong to the same space group is evident from an inspection of their X-ray powder patterns. Therefore, they could differ only in line intensities and, therefore, in details of motif within the unit cell, e.g., silicon, aluminum, and residual cation arrangement, protonic and decationized site arrangement.

Table 1 shows a comparison of ultrastable and normal diffraction patterns, normalized to the same total diffracted intensity. It is clear that whatever differences exist are relatively small and can be accounted for by the small difference in Na^+ cation content, and possibly water, associated with the cation.

Of course, the differences postulated by M & M involve only ionization of hydroxyl linkages and accompanying lattice relaxation. This would be very difficult to detect by X-ray. However, on theoretical grounds, their postulated structures seem less than

satisfactory. Even if the unshielded protons are disregarded, proton tunneling in the temperature range from ambient to $\sim 300^\circ\text{C}$ is rapid enough (14) that, at best, the two structures would represent merely contributing conformations of a tautomeric equilibrium, and not physically resolvable species.

It is interesting to compare the small differences observed in Table 1 with the larger differences seen in Table 2. Table 2 compares the intensity distribution of a sample of cold-exchanged and 340°C -treated material ($\sim 4\%$ Na_2O) with the same sample calcined at 540°C for 2 hr. Here, we have definitely larger intensity differences, indicating structural changes. Since the Na^+ cations in this material are now "accessible" to exchange, as intimated by M & M, it is natural to hypothesize that they have, in fact, moved from their positions at the centers of the double hexagonal rings to other, physically more accessible, locations in the crystal structure, and that this movement to new locations is responsible for the changes involved. A detailed analysis of the observed intensity changes would aid in confirming this hypothesis, and is being attempted.

Few proposals have been made to date

TABLE 2
LINE INTENSITIES OF PARTLY
AMMONIUM-EXCHANGED
SYNTHETIC FAUJASITE
BEFORE AND AFTER
CALCINATION
AT 540°C^a

{hkl}	Intensity (counts/sec)		Difference
	Before	After	
111	524	365	159
220	178	145	33
311	175	150	25
331	220	220	0
333, 511	88	60	28
440	99	105	-6
620	19	20	-1
533	23	30	-7
711, 551	167	170	-3
642	23	25	-2
733	137	150	-13
822, 660	42	40	2
555, 751	80	85	-5
840	148	165	-17
664	49	55	-6

^a Both scans taken at 340°C in flowing dry N₂. Therefore, essentially no ammonium ions were present in either case. Scans are normalized to same total peak intensity after background subtraction.

regarding the mechanism of aluminosilicate structure degradation, due to the paucity of data available. While it is not suggested that a complete, detailed mechanism can now be proposed, some preliminary suggestions seem in order to provide a basis for further discussion. Any proposed mechanism must take account of the set of phenomena comprising segregation of Si and Al species, the presence of octahedrally coordinated Al, the possible presence of trigonal Si⁺, Na⁺ migration, Na⁺ concentration effects, and the presence of intermediate phases.

We suggest a mechanistic picture involving activated electrophilic interaction of sodium with an adjacent Al-O-Si linkage, mediating increased electron localization and establishment of transient trigonal coordination as sodium ion migrates along the surface of the exposed oxygen atoms of the aluminosilicate framework, subject, however, to barriers to diffusion such as grain boundaries. The temporary existence of

trigonal coordination prior to silica and alumina phase separation would allow charge adjustment in the vicinity of the interaction to provide the driving force for activating further sodium attack on a proximally located Al-O-Si bond, or attack by oxygenated species on the trigonal Si⁺ discussed by Uytterhoeven *et al.* (20).

Al-O bonds can be weakened by interaction of Na⁺ with oxygen, to produce trigonal Al. The resulting Na⁺ O⁻-Si linkage can be postulated to interact with Al-O-Si to form Si-O-Si bonds, thus promoting phase segregation. Octahedral Al may be formed from the trigonal Al by inversion through its remaining bonds into the pseudooctahedral cation locations at the $\bar{3}m$ (center of hex-prisms) lattice positions. This inversion would form the basis, with slight rearrangement, for Al-O-Al linkages. This would have some similarity to the hypothesis of Kerr (7). It would conflict, however, with the evidence of Olson and Dempsey (8), who found no cations present after formation of H faujasite. Any cations, including interstitial ones as postulated by Kerr, would have been detected by these authors if the site occupancy were greater than about 0.1.

A larger number of sodium cations would permit a greater degree of Si-O-Al bond breaking prior to the mullitization reaction, giving rise to a difference in heat effects as a function of cation content, as suggested by the curves in Fig. 1. A similar type of relationship is well known for kaolinites with varying degrees of crystallinity, and has been found to hold for other aluminosilicates as well (19, 21). The increase in temperature of mullitization with increasing sodium content may be due to the inhibiting effect of a sodium-enriched glass phase out of which the mullite must nucleate and crystallize (22). Under extreme conditions, i.e., little or no exchange of sodium, it may be difficult or even impossible to detect the presence of mullite after calcination to 1100-1200°C.

The speculative views described above would provide a means of accounting for kinetically controlled thermal destruction at all levels of sodium concentration, in accordance with the limited knowledge extant on the subject. While this is an idealized

picture and does not take into account other possible effects and interactions, it may aid in visualizing the role of sodium in aluminosilicate collapse at elevated temperatures. Since Al-O-Si bonds are thermally ruptured even in the absence of sodium (21), a catalytic type of effect is assumed to be operative.

Two questions remain to be discussed. First, What of the data of M & M regarding widely differing stabilities of normal and ultrastable faujasites of low sodium level? Second, Does the suggested stability mechanism accord with what is known concerning ionic binding and mobility of ions in zeolitic structures?

With regard to the first point, since the faujasite structure has been shown to be metastable at high temperatures and to undergo a kinetically controlled thermal degradation, it is quite possible that small differences in the amounts of impurities present could greatly influence the stability. The loss of zeolite observed possibly may also be due to loss in the exchange process itself. Since, in the present work, conventionally prepared samples with equally low sodium contents were shown to be as stable as samples subjected to intermediate calcination, the concept of uniquely conferring stability via intermediate calcination is open to serious question. The data in Fig. 2 show that the zeolite structural breakdown temperature is essentially identical for the samples exchanged to 0.1% Na₂O, notwithstanding the fact that one was prepared by the M & M procedure and the other by exhaustive conventional exchange. The conventionally exchanged samples were subjected to treatment with ~250 equivalents of NH₄⁺ per equivalent of Na⁺, with no loss in zeolite peak intensity, and were compared under similar pretreatment and scanning conditions.

With regard to the second point, it is known that ionic mobility in zeolite structures can be thermally activated (15). However, it seems quite probable that there is a large energy barrier between different cation sites in the lattice and that mobility of cations in certain sites is quite low at temperatures of ambient to, say, 100°C. Results of X-ray investigations of cation location in

the literature differ somewhat (4, 5, 6). This difference has been attributed by Baur (5) to differences in hydration level of the samples. This may well be correct, but nonetheless, cation equilibration may be a very slow process at low temperatures. If this is true, thermal activation at 540°C, as in the M & M procedure, is merely a question of activated migration of cations out of the double hexagonal rings to more accessible sites for exchange. Thus, low-sodium-content samples prepared by such a procedure would not represent a different crystalline phase from low-sodium-content samples prepared by other means.

It is believed then, that the hypotheses concerning thermally activated cation migration are a valid explanation for the various stability data found to date, and that they are in accord with all that is known about the structure of faujasite. Alternative hypotheses which would be in accord with all the available facts are not readily visualized, although it is recognized that other factors, such as contamination, matrix effects, compositional and evaluational variations, etc., could contribute appreciably to the observed phenomena.

REFERENCES

1. McDANIEL, C. V., AND MAHER, P. K., Conference on Molecular Sieves, Society of Chemical Industry, London, April, 1967; U. S. Patent 3,293,192.
2. BAKER, R. W., MAHER, P. K., AND BLAZEK, J. J., Reprints, Rocky Mountain Regional Meeting, National Petroleum Refiners Assn., Casper, Wyoming, Sept., 1967.
3. ROMANOVSKII, B. V., TKHOANG, K. S., TOPCHIEVA, K. V., AND PIGUZOVA, L. I., *Kinetics & Catalysis (English Transl.)* **7**, 739 (1966).
4. BROUSSARD, L., AND SHOEMAKER, D. P., *J. Am. Chem. Soc.* **82**, 1041 (1960).
5. BAUR, W. H., *Am. Mineralogist* **49**, 697 (1964).
6. EULENBERGER, G. R., SHOEMAKER, D. P., AND KEIL, J. G., *J. Phys. Chem.* **71**, 1812 (1967).
7. KERR, G. T., *J. Phys. Chem.* **71**, 4155 (1967).
8. OLSON, D. H., AND DEMPSEY, E., in press.
9. TURKEVICH, J., AND CIBOROWSKI, S., *J. Phys. Chem.* **71**, 3208 (1967).
10. UYTTERHOEVEN, J. B., CHRISTNER, L. G., AND HALL, W. K., *J. Phys. Chem.* **69**, 2117 (1965).
11. WARD, J., *J. Catalysis* **9**, 396 (1967).

12. MCATEE, J. L., JR., *J. Catalysis* **9**, 289 (1967).
13. KERR, G. T., *J. Phys. Chem.* **72**, 2594 (1968).
14. FRIPIAT, J. J., AND TOUSSAINT, F., *J. Phys. Chem.* **67**, 30 (1962).
15. FREEMAN, D. C., AND STAMIREN, D. N., *J. Chem. Phys.* **35**, 799 (1961).
16. BARNES, R. B., RICHARDSON, D., BERRY, J. W., AND HOOD, R. L., *I&EC (Anal. Ed.)* **17**, 605 (1945); "Scott's Standard Methods of Chemical Analysis" (H. Furman, ed.), 6th ed., Vol. 1, Van Nostrand, Princeton, New Jersey, 1962.
17. TAYLOR, A., AND SINCLAIR, H., *Proc. Phys. Soc. (London)* **57**, 126 (1945).
18. NELSON, J. B., AND RILEY, D. P., *Proc. Phys. Soc. (London)* **57**, 160 (1945).
19. FLANK, W. H., unpublished data.
20. UYTTERHOEVEN, J. B., JACOBS, P., MAKAY, K., AND SCHOONHEYDT, R., *J. Phys. Chem.* **72**, 1768 (1968).
21. KOEHLER, F. K., Second International Conference on Thermal Analysis, Worcester, Massachusetts, Aug., 1968.
22. BARRER, R. M., private communication.