

PROPERTIES OF THE ZEOLITE, FAUJASITE, SUBSTITUTIONAL SERIES: A REVIEW WITH NEW DATA

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Abstract—New information is presented relating to the hydrothermal stability, lattice parameters, and adsorptive, electrical, and catalytic properties of synthetic and natural faujasite. Present concepts concerning the nature and relationship of synthetic and natural faujasite are restated to be consistent with the experimental evidence and the developed physical model. The major structural and physicochemical properties reflect the close similarities and smooth gradations expected of substitutional members of a continuous series. The existing division of the range (2–6) of $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratios (S/A) at 3 into two compositional subranges is shown to be unjustifiable and rather misleading. Individual compositions from these two subranges do not represent distinctly different zeolite species; instead, it is demonstrated that they are members of a continuous series with smoothly changing properties over the studied range of $\text{SiO}_2/\text{Al}_2\text{O}_3$. Some of the properties of the natural mineral faujasite are found to be very similar to those of the synthetic analogs with the same $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio.

Finally, a plea is made for a uniform nomenclature which will serve to identify specific (single) compositions (instead of ranges of compositions); reflect the continuity, close similarities and interrelationships in their main structural and physicochemical properties; and also identify the characteristics of the faujasite group.

INTRODUCTION

HISTORICALLY, experimental work on crystalline aluminosilicates of the faujasite type started when Damour (1848) published a chemical analysis of faujasite. Synthetic zeolites designated as X and Y were produced by Milton (1959) and Breck (1964). The X-ray work of Baur (1964), Bergerhoff *et al.* (1956) and Broussard and Shoemaker (1960) and the adsorption studies of Barrer *et al.* (1957) established the structural identities of these synthetic zeolites and the natural mineral. However, the location of certain cations in the aluminosilicate framework and the relative degree of (Si, Al) ordering in the lattice still remain uncertain and may be different in the synthetic and natural species.

It is possible to synthesize hydrothermally a continuous series of faujasite zeolites with uniform compositional variation. Breck (1964) has divided this series into two compositional ranges, one a high alumina species designated as type X, the other a high silica species designated as type Y. Over the entire silica–alumina range from 2–6, the unit cell dimensions for zeolites in both ranges were found (Breck and Flanigen, 1968) to vary linearly

with the degree of replacement of Si by Al in the crystal framework. A $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio (hereafter referred to as S/A) of three was chosen (Breck, 1964) as the boundary between type X and type Y. It has also been stated (Breck, 1964) that Zeolite X is distinctly different from Zeolite Y and that both are different from natural faujasite. Thus, according to this scheme, there occurs within the substitutional series three distinctly different zeolite species; namely, X, Y and natural faujasite. To justify this distinction Breck (1964) stated that X-ray data (structural properties) had to be considered together with other properties, such as chemical composition, hydrothermal stability, adsorption, and ion exchange.

This paper reviews the earlier work and presents new information which establishes the close similarity in the hydrothermal stability, adsorption and other properties of both synthetic and natural faujasite. It is also shown that there is no justification within these properties of the substitutional series to warrant a division at a S/A of three, or at any other point.

The main criteria used by Breck (1964) for the

distinction between X, Y and natural faujasites were hydrothermal stability, ionic conductivity, and sorption properties. In this paper, these same properties and additional structural data support the lack of any such distinction and demonstrate the similarities in the properties of the substitutional members of the faujasite series. Further, these new data should help resolve the conflicts in the conclusions of Breck (1964); Dempsey, Kühl and Olson (1969); Wright, Rupert and Granquist (1968, 1969); recently summarized by Smith (1971).

MATERIALS AND METHODS

The zeolites were synthesized from pure chemicals by the procedures of Barrer (1959); Milton (1959) and Breck (1964). Samples were analyzed by X-ray diffraction and fluorescence, chemical analysis, and by the electron microprobe. Repeat preparations were made at each desired composition, and those samples with the highest crystallinity and most uniform crystals were selected for the detailed study. Special care was taken to eliminate occlusion of free sodium silicate in the zeolite crystals. The $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ mole ratio was kept close to unity by ion exchange with NaCl. The selected zeolites contained less than 20 ppm Fe and less than 80 ppm Ca and Mg. The S/A was determined both by wet chemical analysis and by X-ray fluorescence.

The samples usually were activated by room temperature desorption under vacuum for several hours followed by a slow temperature increase (about $2^\circ\text{C}/\text{min}$) to the $400\text{--}450^\circ\text{C}$ range where the samples were kept at approximately 10^{-7} torr for periods of 8–16 hr until the dehydration was complete. A McBain balance and a mass spectrometer were used routinely to establish complete dehydration of the samples and to avoid unnecessarily prolonged heating. The samples with higher Al contents required longer heating under vacuum to release the last traces of water.

The X-ray measurements were done with $\text{CuK}\alpha$ radiation at scanning rates of 2° and $0.25^\circ 2\theta/\text{min}$. An average value of the unit cell parameter a was obtained from several diffraction peaks for each sample. The θ values were corrected by the known reflections of either NaCl or metal oxides, which were mixed together with a portion of zeolite sample.

Ion exchange was usually done by percolation; i.e. a concentrated solution of the salt of the exchanging ion was allowed to flow through the zeolite sample.

EXPERIMENTAL RESULTS AND DISCUSSION

Hydrothermal stability

The hydrothermal stability of each sample, over a wide range of S/A, was determined and compared with results available in the literature. In order to make the comparison valid, the same experimental conditions (Breck, 1964) were used: steaming the samples at 410°C and atmospheric pressure for 3 hr. The steamed samples were activated by heating at 460°C and 10^{-7} torr by the monitoring procedure already described. Oxygen sorption capacity at -183°C and 100 torr was measured on each sample before and after steaming.

Four samples of the same S/A were studied to establish the reproducibility of the method. The first few experiments indicated that a steaming period of 3 hr was not sufficient and that up to 5 hr was required to obtain equilibrium. Oxygen sorption capacities and X-ray intensities of the steamed samples were used to establish this equilibrium. Non-reproducible results were obtained with commercial synthetic faujasite with Fe-content in the range of 0.05–0.1 per cent and with samples containing appreciable occluded sodium silicate; i.e. non-reproducibility correlated with impurity content. Preliminary results indicate that both iron (which on heating forms the ferromagnetic species Fe_3O_4 , Singer and Stamires, 1965) and occluded sodium silicate enhance the hydrothermal decomposition of the crystalline zeolite. Thus, the presence of these impurities causes a considerable variation in the stability data.

A sample of natural faujasite (Kaiserstuhl occurrence) was included for comparison with the series of synthetic samples. The sample was converted to the sodium form (remaining Ca and Mg was less than 0.03 weight per cent) by repeated ion exchange, and ground to a fine powder before use.

The results are presented in Fig. 1, where the percent crystallinity retained after steaming is plotted as a function of S/A. For comparison, the data of Breck (1964) are also shown. All data were correlated using third degree polynomials to determine the r.m.s. deviation, and the most probable values. These results also appear in Fig. 1.

Although it is questionable if statistical treatment of the Breck (1964) data is justifiable because of the large spread, it is interesting to note that the smooth curve obtained from the correlated data closely resembles that of the new equilibrium results. Thus, it can be concluded that a smooth continuous curve is indeed the best representation for the data. The plot of the new equilibrium results, without the large spread of data, lies generally below the Breck

curve, as would be expected from the increased severity of the steaming process. The plots converge at ratios near 5. The position of the natural faujasite in the plot is in accord with its composition. Thus, the stability data demonstrate the existence of a continuous substitutional series with natural faujasite as a member.

The crystallinity remaining in these samples after steaming was also measured by X-ray diffraction techniques and was found to vary with the S/A in much the same way as the retained crystallinity shown in Fig. 1.

Mechanism of structural degradation by steaming

The drastic changes induced by steaming can be viewed as similar to the changes occurring during the heating of NH_4^+ -exchanged faujasite. The hydrolysis of the $(\text{AlO}_{4/2})^- \text{Na}^+$ site results in the formation of a hydroxyl group associated with the $(\text{AlO}_{4/2})^-$ tetrahedron. The distribution of the charge density in the hydroxyl group varies according to its location and crystal environment. In the high alumina members of the series where there are a large number of Na^+ cations on type (iii) sites (Breck and Flanigen, 1968), the hydrolysis results in the production of a substantial number of protons in the supercage. These protons are probably as-

sociated with the oxygen 4-membered rings which constitute very weak cation sites. This association in turn makes these protons very reactive, to the extent that they can hydrolyze part of the aluminosilicate framework. At the same time, some of the Na probably migrates into the sodalite cages, or disperses in the remaining portion of the crystals.

The mechanism by which these chemical changes proceed has been ascertained earlier (Szymanski, Stamires and Lynch, 1960; Rabo *et al.*, 1960) and further substantiated by Uytterhoeven, Christner and Hall (1965).

In addition, Stamires (1965) has studied the e.s.r. spectra of stabilized atomic hydrogen produced by γ -irradiation of synthetic zeolites and the interaction of such hydrogen with the crystal lattice at liquid helium or nitrogen temperatures. In the present work, the e.s.r. spectra of samples, exposed to steam only for short periods followed by vacuum activation at 460°C and γ -irradiation, showed a large amount of hydrogen atoms present. This hydrogen is introduced by the replacement in the structure of some Na^+ by protons resulting from the steam hydrolysis. Then, the protons react with the lattice oxygens to form hydroxyl groups which further by radiolysis produce hydrogen atoms and lattice-oxygen radicals. In high-Al samples, the hyperfine splitting constant of the spectrum of adsorbed atomic hydrogen is smaller (approximately 498 G) than the value of approximately 508 G for the free hydrogen atom. No changes were observed in the G-values; however, the line width increased with decreasing silica content. The broadening is attributed to unresolved hyperfine lines resulting from a distribution of various trapping sites (Stamires and Turkevich, 1964; Stamires, 1968) within the unit cell. As the overall effect observed in the e.s.r. spectra includes both short and long term interactions, (Stamires and Turkevich, 1963) it appears that the distribution of the strengths of the individual hydroxyl groups probably varies from one cell to the other. However, the largest differences are observed among the extreme members in the silica-alumina range investigated.

The decrease in the hyperfine splitting constant is attributed to the strong electric field in the supercage produced primarily by the high density of surrounding protons and sodium ions. The close proximity of the $(\text{AlO}_{4/2})^-$ sites with which the hydrogens are associated and the high reactivity of those hydrogens are responsible for the structural changes in the crystal. The strong electric field in the supercage tends to expand the electronic wave

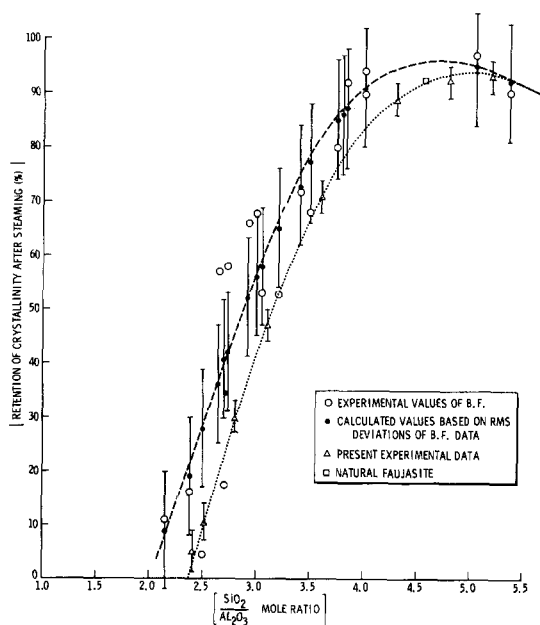


Fig. 1. Variation of hydrothermal stability with varying $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio. Experimental values of Breck (1964), these data after statistical analysis and correlation, and new equilibrium results.

function of the unpaired electron in the hydrogen atom so as to decrease the charge density at the nucleus, and hence to decrease the hyperfine constant. However, when hydrogen atoms are produced on steamed samples with very low alumina contents, the concentration of atomic hydrogen is considerably smaller and the hyperfine constant is closer to that of free atomic hydrogen (approximately 504 G). From electrostatic considerations, it appears that the center of the sodalite unit would be a suitable trapping site for such types of hydrogen.

In some faujasite samples with intermediate S/A, the e.s.r. spectra showed a doublet with hyperfine lines corresponding to the two extreme cases discussed above; i.e. hydrogen atoms trapped in the supercage and in the sodalite unit. Although the appearance of this doublet allows a gross distinction to be made between hydrogens located in these two different sites (these two sites could be identified with those found in the i.r. work corresponding to the 3550 and 3650 cm^{-1} absorption frequencies), the unresolved hyperfine structure of the individual lines of the doublet indicates that there is still another distribution of sites within the individual sodalite and supercage units. This conclusion is in contrast to the information obtained from i.r. (Uytterhoeven, Christner and Hall, 1965) and X-ray diffraction (Olson and Dempsey, 1969), where only two types of hydrogen have been identified (those associated with the O3 and O1 lattice oxygens).

The resolution of i.r. is limited when applied to polycrystalline solids, particularly in cases where the perturbation on some of the hydrogens, produced by the electric field of the environment, is relatively small. In that case small shifts, due to second order effects in the hydroxyl bands, will not be seen in the i.r. spectra. Further, X-ray analysis in itself is not sensitive enough to locate and differentiate the structural positions of the hydrogen atoms. Earlier conclusions regarding the positions of the hydrogens were based on indirect information in X-ray studies.

The exchange of sodium for hydrogen ions induced by steaming appears to produce the same type of product as the thermal activation of the corresponding NH_4^+ form. Based on similarities in the e.s.r. spectra, a similar mechanism for the formation of hydrogen and its stabilization in the zeolite structure appears to operate also in the case of the NH_4^+ faujasites during their thermal activation. However, both the width of the e.s.r. lines and hyperfine splitting constants were found to be strongly dependent on the activation temperature

and purity of the zeolite crystals. A detailed discussion of the e.s.r. spectra of atomic hydrogen in synthetic faujasites will be presented elsewhere (Stamires, in press). However, it is worth mentioning here that hydrogen in the high silica samples is stabilized in the smaller cavities (sodalite units). Due to the relatively weak electric field and large separation between the $\text{AlO}_4(\text{O})^-$ units, the hydrogen in this environment is considerably less chemically reactive. In contrast, hydrogen trapped in the supercages of the high-alumina members of the series is more reactive and is responsible for the destruction of the crystal. In samples with intermediate or low Al content, some of the Na and probably the protons can be stabilized in the small cavities; thus, some of the crystallinity is retained.

In other cases, when the hydrolyzed zeolite is in physical contact with another aluminosilicate phase, such as kaolinite or halloysite, both the excess sodium and hydrogen probably diffuse and become stabilized in the non-zeolite phase. These effects, which probably involve ion exchange, diffusion and hydrolysis in the solid state, are enhanced by the hydrothermal conditions. This change in reactivity is illustrated by the variation with Al-content of the steam stability curve. The substitution of Si for Al in the structure results in a gradual increase of steam stability of the zeolite samples, as shown in Fig. 1. Similar behavior is to be expected in the variation with Al-content of the thermal stability of the NH_4^+ -exchanged faujasite series.

Ionic conduction

Stamires (1960, 1962); Freeman and Stamires (1961); Schoonheydt and Uytterhoeven (1969) have shown that the current-carrying species in synthetic zeolites are cations migrating in the structure by a "jump" mechanism. Further, the activation energy for conduction is due to the electrostatic interaction of the cation with its site in the aluminosilicate framework. This situation is particularly applicable in cases where a relatively small ion (for example, Na), is located in an open framework which has a very minor steric effect on the migration of the cation in that structure. Since the negative charge of a cation site must be distributed over the oxygens bound to a given aluminum, the geometrical configuration of the cation/cation-site pair determines the magnitude of the coulombic interaction. In this case, the configuration should be anisotropic with respect to the unit cell diagonal.

From X-ray investigations (Broussard and Shoemaker, 1960; Breck, 1964) it has been established that the sodium ions in faujasite have at least

two different crystallographic positions. For example, in high-Al-faujasites, 16 Na ions are located within the hexagonal prisms [type (i)] of the double-5 member oxygen rings, and 32 Na ions are associated with the single-6 member oxygen rings [type (ii)]. The rest of the Na ions have been assumed to reside on the surface of the large cavities, probably associated with the four member oxygen rings [type (iii)]. Simple electrostatic calculations reveal* that ion-framework coulombic interactions for sodium ions located in these three discrete crystallographic locations (specifically, the interaction of an Na ion associated with a double 6-member oxygen ring, a single 5-member ring and a 4-member oxygen ring) should be considerably different (Dempsey, 1968).

By synthesis of a series of zeolites, the cation density can be uniformly decreased by decrease in the Al substitution. In this way, the cation population of one or more of the three cation sites mentioned above can be preferentially depleted. A corresponding variation should occur in the activation energy required for the overall conduction process. Briefly, Na ions located on the surface of the large cavities (associated with the 4-member oxygen rings) are the least strongly bound and will therefore require the least amount of energy to migrate. In zeolites with high cation densities, the rate determining process for the migration of the current carriers in an external electric field is due to such weakly bound cations. As the cation density is decreased towards the high silica end of the series, the low energy cation sites are depleted, and the more strongly bound cations start to contribute and hence determine the rate of the conduction process. Consequently, the change in the activation energy for conduction is a direct measure of the differences in the energy associated with the different kinds of cation/cation-site pairs.

*A simplified model of the location of cations in the unit cell is considered; namely, the association of Na ions with double 5-member oxygen rings, single 5-member oxygen rings and 4-member oxygen rings. However, projection through the sodalite unit and the supercage results in actual sites of type (i)' and (ii)', located within the sodalite unit. Type (i) located in the hexagonal prism, type (ii) located in the supercage and type (iii) also in the supercage. In particular, we are concerned here with the difference in the bonding energy of the Na ions in the type (iii) location which is the least stable position (due mainly to the very small coulombic interaction) as compared to the bonding energy at the type (i) and (ii) sites which are considerably more stable, with higher energy of interaction.

†This probably is the average of the individual contributions, such as coulombic, repulsive, polarization and small amounts due to steric effects.

In zeolites with low cation densities, the Na ions are primarily associated with the single and double 6-member oxygen rings; therefore, the activation energy is considerably higher. This situation was shown in the results published earlier (see Fig. 3, of Freeman and Stamires, 1961) which illustrate the uniform change in energy† associated with cation/cation-site pairs among the different crystallographic sites. It was on this basis that a physical model was developed and on purely energetic considerations it was possible to differentiate the cations in the synthetic faujasite into three types. However, Breck (1964) and Breck and Flanigen (1968) have concluded that these data provide evidence for dividing the substitutional series at an S/A of three into two sub-groups, designated as X and Y. In fact, there is a smooth variation in the activation energy with S/A, with no detectable discontinuity. The inflection point (the point where the activation energy changes most drastically with cation density) in the conductivity-Al content plot is close to an S/A of 4, not 3. This point is convincingly illustrated if the first derivative of the activation energy is plotted against the S/A.

In Fig. 2 the activation energy (ΔH) and its first derivative are plotted against S/A. The arbitrary division at a ratio of 3 is also indicated. These data clearly show that such a division is not justified.

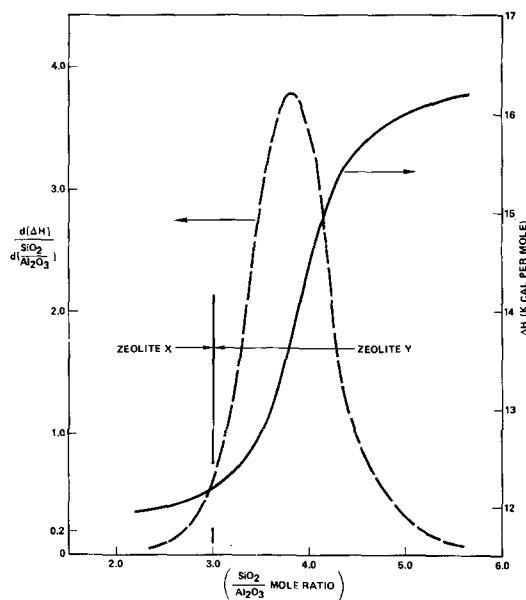


Fig. 2. Faujasite conductivity as a function of silica-alumina ratio, Freeman and Stamires (1961). The broken line represents the plot of the first derivative of (ΔH) with respect to $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio.

Furthermore, the distinction of *X* from *Y* as two different zeolite species (where *X* and *Y* refer to compositional ranges), certainly is not suggested by the results. If one had to use the conductivity data to divide arbitrarily the series into two groups, then an *S/A* of approximately 4 would be a logical choice, since in this region the conduction process changes most drastically with cation density.

As in the case of steam stability, the electronic properties of synthetic faujasites also vary uniformly and continuously with composition.

Adsorption properties

A most important property, which has been used extensively to characterize the various zeolite species, is the adsorption of gases and vapors. Triethylamine adsorption has been used by Breck to distinguish calcium-exchanged Zeolite *X* from similarly treated Zeolite *Y*. Further, Wright, Rupert and Granquist (1969), hereafter referred to as *WRG*, have reported similar experiments using the Na forms of two synthetic faujasites with *S/A* of 2.4 and 4.8.

In the present work, the measurements have been extended to cover the whole range of *S/A* and to include a sample of natural faujasite in its sodium form. Equilibrium data were obtained from experiments where the adsorption of triethylamine at room temperature was measured as a function of vapor pressure. Equilibrium was reached, at the lower vapor pressures, after 8–10 hr. In order to compare *WRG* and present results, the same experimental conditions were used. The data are cross-plotted in Fig. 3. All the samples studied adsorbed about the same amount of triethylamine, within experimental error. Since the size of the unit cell decreases with *S/A*, adsorption would be expected to decrease with increasing *S/A*. Probably the variation in the number and distribution of the cations in the unit cell offsets this trend. The important point to note here is that all the samples, including natural faujasite, show (within experimental error) about the same adsorptive capacity. The two measurements reported earlier by *WRG* are in agreement with the present results.

Accordingly, a division based on the adsorption of triethylamine of the substitutional series at any *S/A* in the range 2–6 is not justifiable. Further, natural faujasite cannot be distinguished as a different type of zeolite on the basis of such data. Similarly, the adsorptive capacities of the substitutional series and natural faujasite for oxygen and water at -183°C and at room temperature respectively (at the same vapor pressures), within the experimental

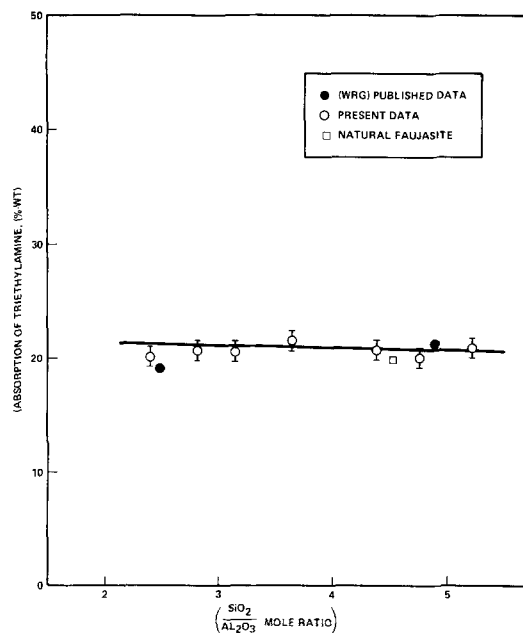


Fig. 3. Equilibrium capacity for triethylamine adsorption at 3 torr and room temperature as a function of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio.

error, were found to be about the same. Thus, the pore volume, as indicated by these adsorptive capacities, is about the same in the synthetic and natural members of the faujasite group.

It is very important in comparing the various physicochemical properties of the substitutional series of faujasites to use the same homocationic forms in the experiments. The type of cation (sizes and charge) and the percent exchange affect drastically the adsorption characteristics of the zeolite crystals. The data presented by Breck (1964) on the triethylamine adsorption by synthetic faujasites were on calcium forms (approximately 85 per cent exchanged).

Variation of unit cell dimension with composition

The replacement of aluminum for silicon in the structure has been discussed by Breck (1964). From simple geometrical considerations of the Si–O and Al–O bond distances (i.e. 1.605 and 1.757 Å, respectively), it is expected that the cubic lattice parameter *a* should decrease smoothly with increasing *S/A*. This general concept was illustrated by Breck and Flanigen (1968), hereafter referred to as *BF*, who examined 37 samples of synthetic faujasites of varying *S/A*. They have shown by a least square fit that *a* varies linearly with the number of Al atoms in the unit cell. *BF* reported an experimental error

of $\pm 0.005 \text{ \AA}$ in a and $\pm 0.5 \text{ wt\%}$ in the silica and alumina contents.

More recently, *WRG* reported a values for synthetic faujasites synthesized from hydrous sodium systems similar to those used by *BF*. The estimated probable error in the data of *WRG* was ± 0.01 in a and $\pm 0.005 \text{ \AA}$ in the mole fraction of AlO_2^- . In the paper of Freeman and Stamires (1961), several a values were also given for synthetic faujasites. These data were obtained in the very early stages of faujasite synthesis and the techniques for a and S/A determination were not yet well refined; therefore, the experimental error was larger, close to ± 0.2 in the S/A values.

In this work, samples were synthesized and studied in a manner similar to the work of *BF* and *WRG*. The estimated probable error in the present data is ± 0.1 in the S/A and $\pm 0.005 \text{ \AA}$ in the a values.

The results are compared in Fig. 4. Within the experimental variation, there is agreement between the results of these four independent groups. These studies represent work done over at least the last 10 yr, with various analytical techniques and levels of sophistication. *BF* (1968) reported precision methods for determining a which are used routinely to identify faujasite samples.

BF also presented data on a values of dehydrated calcium-exchanged synthetic faujasites. In contrast to the hydrated sodium forms, a in this case did not vary linearly with S/A, and the data

displayed two discontinuities, at approximately 62 and 77 Al per unit cell. These discontinuities were interpreted by *BF* as due to framework distortion associated with movement of Ca ions. Dehydration causes the calcium ions to move to structural positions which are more favorable energetically. The mechanism responsible for these discontinuities may be much more complicated than described, since the samples contained appreciable amounts of residual Na, and since heating in air at 400°C is not the best way to activate calcium-exchanged zeolites. Also, if a values for Na and Ca forms of the same samples are compared, a also changes as Na is exchanged for Ca in samples containing the same amount of Al. This dependency introduces another variable, degree of ion exchange, into the determination of a . However, the important factor to be noted here is that the techniques used by *BF* were sensitive and quite reliable in order to be able to establish these differences in the a values.

Despite the agreement shown in Fig. 4, a complication is introduced by the results of Dempsey, Kühl and Olson (1969), hereafter referred to as *DKO*, who have also studied the variation of a with Al content for hydrated Na-faujasite. In contrast to all previously published data, *DKO* found three discontinuities in a , near 52, 64, and 80 Al atoms per unit cell. *DKO* suggested that at least three different faujasite phases exist in the S/A range studied. The discontinuity observed at the highest Si content was assumed to be due to the presence of

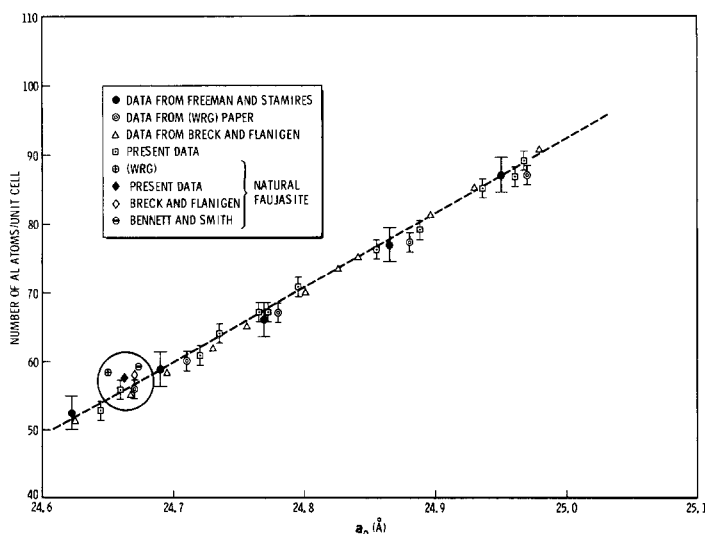


Fig. 4. Variation of the lattice parameter a with aluminum content for synthetic and natural faujasite in the hydrated sodium (homocationic) form. Data of Breck and Flanigen (1968); Wright, Rupert and Granquist (1968); Freeman and Stamires (1961), and the present results. a values for natural faujasite are shown enclosed in a circle for emphasis.

amorphous silica occluded in the samples. *DKO* do not describe the techniques used in synthesizing their samples. However, if they used the teachings of Barrer (1959) and Breck (1964) for the synthesis of faujasites, then their data would be expected to be similar to the results, in Fig. 4, of *BF*, *WRG* and the present paper. Further, it is highly improbable that their observed discontinuities represent experimental artifacts. These irregularities probably represent real effects characteristic of the nature of the *DKO* samples. In the absence of additional information, it must be concluded that this discrepancy is due to differences in the *DKO* samples caused by variations in synthesis and preparation techniques.

DKO explain these discontinuities on the basis of variations in (Si, Al) ordering. Since such ordering will tend to decrease a , the fact that all the *DKO* data lie below the straight line of Fig. 4 suggests that the samples used by *BF*, *WRG* and the present author correspond to higher (Si, Al) ordering. Further, the a data indicate that natural faujasite has the highest order. Three previously reported values of a for the natural mineral and the present measurement are shown in Fig. 4. The present result was obtained on hydrated homocationic Na-faujasite crystals which were used in the other experiments described in this paper. S/A was found to be 4.55 ± 0.01 and the cubic lattice parameter a , 24.66 ± 0.005 Å; these values were established after several determinations. These values are very close to those of *BF* and Bennett and Smith (1972). All four values are presented in Fig. 4, enclosed in a circle for emphasis. The *BF* value of a lies close to the straight line obtained from the a values for the synthetic samples. In all cases, the natural crystals appear to be more (Si, Al) ordered than the synthetic material, probably due to more ideal natural growth conditions. Although reasonable, there is no direct experimental evidence to substantiate this postulated ordering.

The a values shown in Fig. 4 represent about 60 samples synthesized and analyzed independently by four or five groups of workers at different times. It can be concluded that when faujasites are synthesized by standard procedures (Barrer, 1959, Breck, 1964), then the a values vary linearly and correlate quite well with the aluminum content of the crystals. Two out of the four reported values of a for natural faujasite are, within the experimental error, close to the straight line obtained for the synthetic samples. Nevertheless, to a first order approximation insofar as the variation of a with Al content is concerned, it can be concluded that the

difference between natural and synthetic samples is quite small.

The location of the charge-balancing cations in the structure, the (Si, Al) ordering, and the distribution of the adsorbed molecules may be different in the natural and synthetic samples.

From a statistical point of view, the data presented in Fig. 4 (particularly the *BF* and present results) appear to be in accord. Despite this accord, the conflicting *DKO* results show that the variation of a with composition is not a closed issue. Further exploration is necessary to yield a definitive answer.

Catalytic properties

Catalytic behavior, although complicated to ascertain, is another characteristic property of the substitutional series. The main factors which determine the performance of a zeolite catalyst are: silica-alumina ratio; percent exchange and nature of the exchange cation; method of preparation; and type of matrix (the zeolite is usually contained in supporting matrix). Good catalysts have been prepared from faujasites with both high- and low-Al contents.

Kimberlin and Gladrow (1961) demonstrated excellent catalytic properties of zeolitic catalysts using synthetic faujasite with S/A of 2.7. Subsequently, Rabo *et al.* (1966) published results on catalytic properties of synthetic faujasites with S/A in the range 3–6, and claimed that the catalytic properties of these zeolites were unique and different from those studied by Kimberlin and Gladrow (1961). This assertion was in line with Breck's concept that Y zeolite is different from X. Both of these groups of workers failed to indicate the percent error involved in the S/A used in their claims.

As is shown in Fig. 5, the catalytic activity, for cracking cumene at 400°C, of a series of Mg exchanged faujasite catalysts varies smoothly with S/A. The techniques used for these catalytic measurements were similar to those of earlier studies (Turkevich, Nozaki and Stamires, 1964) where other types of zeolite catalysts were investigated. A discussion of the mechanism involving the effect of S/A on the catalytic activity and other related physical and structural properties is beyond the scope of this paper and will be presented elsewhere (Stamires, to be published). The issue considered here is the fact that catalytic activity for cumene cracking (within the experimental error) varies almost linearly with S/A in the range of 2–4. Similarly, a linear variation is observed in the range of 4–6. Alternatively, one could represent the whole range

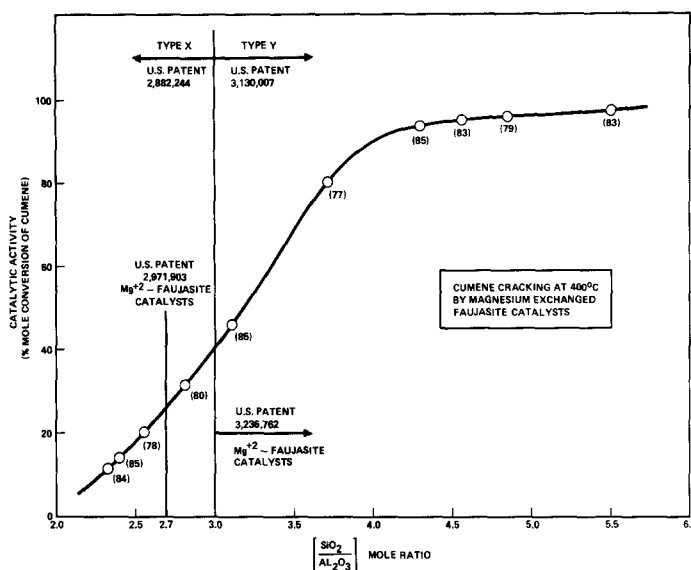


Fig. 5. Variation of the catalytic activity for cumene cracking at 400°C with silica-alumina ratio. The samples were activated at 450°C prior to catalytic measurements.

studied (2–6) by two straight lines corresponding to the two ranges (2–4) and 4–6) and intersecting approximately at S/A of 4.

The continuous variation of catalytic activity with no discontinuity at S/A of 3 is in accord with the other properties discussed earlier. Catalytic activity for other types of hydrocarbon reactions may show a different type of dependence on the S/A; however, a sharp discontinuity at 3 in the S/A (2–6) range is unlikely.

CONCLUSIONS

Critical review of the literature and new studies, described in this paper, establish the smooth, continuous variation with composition (Al-content) of the following properties of a substitutional series of synthetic faujasites:

- (1) Retention of crystallinity upon steam-degradation at 410°C;
- (2) Activation energy of the conduction process;
- (3) Equilibrium adsorption of triethylamine;
- (4) Unit cell dimension, a ; and
- (5) Catalytic properties, particularly the cracking of cumene.

On the basis of steam-stability, triethylamine adsorption, and a vs composition, the natural counterpart (Kaiserstuhl occurrence) is shown to be a member of the series, although perhaps more highly-ordered.

The conflict between the discontinuities shown by DKO and the line of Fig. 4 (based on BF, WRG,

Freeman and Stamires, and the present writer) is unresolved. Additional work at a still higher level of sophistication will be required for a definitive answer.

Further, faujasite samples synthesized with similar hydrothermal techniques show consistent a values at a given composition, and a varies linearly with the aluminum content of the crystals.

In the light of these facts, this writer proposes that the existing artificial division of the faujasite series at a S/A of 3 be eliminated, and a new nomenclature adopted. This new nomenclature should be capable of representing precisely one particular composition, rather than the wide range of compositions encompassed by the trade names presently in use. Further, this new nomenclature should clearly reflect the actual similarities and the smooth gradual variation in the most important physicochemical properties of the continuous series and the close similarities with their natural counterpart faujasite.

Such a uniform system for naming the various zeolite members in the continuous substitutional faujasite series could be one similar to that already suggested by WRG.

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Résumé—On présente dans ce travail de nouvelles informations se rapportant à la stabilité hydrothermale, les paramètres de réseau, les propriétés d'adsorption et les propriétés électriques et catalytiques d'échantillons de faujasite synthétique et naturelle. Les concepts actuels concernant la nature et les relations existant entre la faujasite synthétique et la faujasite naturelle sont repris pour être en accord avec les preuves expérimentales et le modèle physique développé. Les propriétés structurales et physico-chimiques principales reflètent des similitudes étroites et des gradations régulières que l'on peut attendre entre des termes de substitution qui forment une série continue. On divise actuellement le domaine des rapports molaires $\text{SiO}_2/\text{Al}_2\text{O}_3$ (S/A), qui s'étend de 2 à 6, à la valeur 3; cette division en deux sous domaines de composition apparaît non justifiée et risque plutôt d'induire en erreur. Les compositions individuelles prises dans ces deux sous domaines ne représentent pas des types de zéolites distinctement différents; en réalité, on démontre qu'il s'agit de termes d'une série continue, avec des propriétés changeant graduellement sur toute l'étendue $\text{SiO}_2/\text{Al}_2\text{O}_3$ étudiée. Certaines des propriétés de la faujasite naturelle ont été trouvées très semblables à celles d'analogues synthétiques ayant le même rapport molaire $\text{SiO}_2/\text{Al}_2\text{O}_3$.

Finalement, on exprime le voeu que soit créée une nomenclature uniforme qui servira à identifier des compositions spécifiques (uniques) au lieu de domaines de compositions à rendre compte de la continuité, des similitudes étroites et des interrelations dans les propriétés structurales et physico-chimiques principales à identifier également les caractéristiques du groupe de la faujasite.

Kurzreferat – Neue Erkenntnisse bezüglich der hydrothermalen Stabilität, der Gitterparameter, sowie der adsorptiven, elektrischen und katalytischen Eigenschaften von synthetischem und natürlichem Faujasit werden mitgeteilt. Gegenwärtige Vorstellungen, die die Natur und das Verhältnis von synthetischem und natürlichem Faujasit betreffen, werden als im Einklang mit den experimentellen Ergebnissen und dem entworfenen physikalischen Modell befunden. Die wichtigsten strukturellen und physikochemischen Eigenschaften spiegeln die große Ähnlichkeit und den fließenden Übergang wider, die für die Substitutionsglieder einer kontinuierlichen Reihe zu erwarten sind. Die bestehende Aufteilung des Bereiches (2 bis 6) der $\text{SiO}_2/\text{Al}_2\text{O}_3$ -Molekularverhältnisse (S/A) bei 3 in zwei Unterbereiche der Zusammensetzung wird als ungerechtfertigt und eher irreführend hingestellt. Die individuellen Zusammensetzungen innerhalb dieser beiden Unterbereiche stellen keine eindeutig verschiedenen Zeolith-Arten dar. Es wird vielmehr gezeigt daß sie innerhalb des untersuchten $\text{SiO}_2/\text{Al}_2\text{O}_3$ -Bereiches Glieder einer kontinuierlichen Reihe mit fließend wechselnden Eigenschaften sind.

Einige der Eigenschaften des natürlichen Minerals Faujasit erwiesen sich als denjenigen der analogen synthetischen Minerale mit dem gleichen $\text{SiO}_2/\text{Al}_2\text{O}_3$ -Molekularverhältnis sehr ähnlich.

Schließlich wird für eine einheitliche Nomenklatur eingetreten, die dazu dienen soll, spezifische (Einzel-) Zusammensetzungen (an Stelle der Zusammensetzungsbereiche) zu identifizieren, die Kontinuität sowie die große Ähnlichkeit und die engen Wechselbeziehungen ihrer wichtigsten strukturellen und physikochemischen Eigenschaften widerzugeben und die Merkmale der Faujasit-Gruppe zu bestimmen.

Резюме — Приводится новая информация относительно гидротермической стабильности, параметров решетки, адсорбции, и о электрических и каталитических свойствах синтетического и естественного фюзита. Современное представление о соотношении синтетического и естественного фюзита вновь формулируется, чтобы оно соответствовало экспериментальным доказательствам и разработанной физической модели. Главные структурные и физикохимические характеристики отражают близкое сходство и гладкие градации, которые можно ожидать от замещаемых элементов непрерывной серии. Существующее разделение классификации (от 2 до 6) $\text{SiO}_2/\text{Al}_2\text{O}_3$ с мольным отношением (S/A) в 3 на два оказывается неоправдывается и вводит в заблуждение. Индивидуальные текстуры этих двух подгрупп не представляют ясно различающихся цеолитовых пород; зато продемонстрировали, что они являются членами непрерывной серии с гладко переходящими характеристиками, как видно по изученному $\text{SiO}_2/\text{Al}_2\text{O}_3$. Нашли, что некоторые характеристики естественного минерального фюзита очень похожи на синтетическую модель с тем же мольным отношением $\text{SiO}_2/\text{Al}_2\text{O}_3$.

В заключение выдвигается предложение на единообразную терминологию, которая может служить для идентификации характерной композиции (вместо ряда композиций); и отразит непрерывность, близкие сходства и взаимоотношение в их главных структурных и физико-химических свойствах, и также идентифицирует особенности фюзитной группы.