

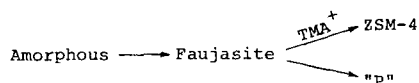
ZSM-4 Crystallization via Faujasite Metamorphosis

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The crystallization of ZSM-4 via faujasite metamorphosis has been studied by X-ray diffraction and scanning electron microscopy. By the addition of tetramethylammonium (TMA) ions, the well-known transition from metastable faujasite to "P" zeolite was directed to ZSM-4 zeolite instead. The following reaction sequence was observed for these crystallizations:



There is no indication of a simultaneous or competitive crystallization since no ZSM-4 is formed until the faujasite crystallization is complete. Also, there is no evidence to indicate that the faujasite reverts to an amorphous material which might serve as a nutrient source for the recrystallization to ZSM-4. Scanning electron microscopic observations are consistent with a mechanism that would include a dissolution of surface faujasite crystals that supplies nutrient for the ZSM-4 crystallization which, in turn, is nucleated by the surface of the same faujasite crystals.

INTRODUCTION

The metastable nature of many crystalline aluminosilicate zeolites is well known and documented. In fact this metastable character has been proposed as an explanation of the nonexistence in nature of many of the zeolites that have been synthetically prepared. This metastability of zeolites is seen in the transformation from one crystal structure to another and in differences in ordering within a given crystal structure. The rate at which the metastable zeolite changes to an equilibrium or more stable material is dependent upon intrinsic properties of the zeolite, and the chemical environment in which it exists. As an example, as Breck (1) points out, if zeolite A after crystallization is allowed

to remain in its mother liquor it will recrystallize to zeolite P. In the crystallization of zeolites X and Y, which are also metastable to zeolite P, it has been shown that changes in the composition of the amorphous reaction mixture, the source of SiO₂, and temperature of crystallization can promote the formation or recrystallization to zeolite P and ultimately analcime.

The work presented in this paper treats the transition from amorphous aluminosilicate gel to Y-type faujasite to ZSM-4 (2, 3), a large-pore zeolite containing tetraalkylammonium cations as well as sodium cations, with a SiO₂/Al₂O₃ somewhat greater than that of the Y-type faujasite, and a distinctly different crystal structure and morphology. As previously

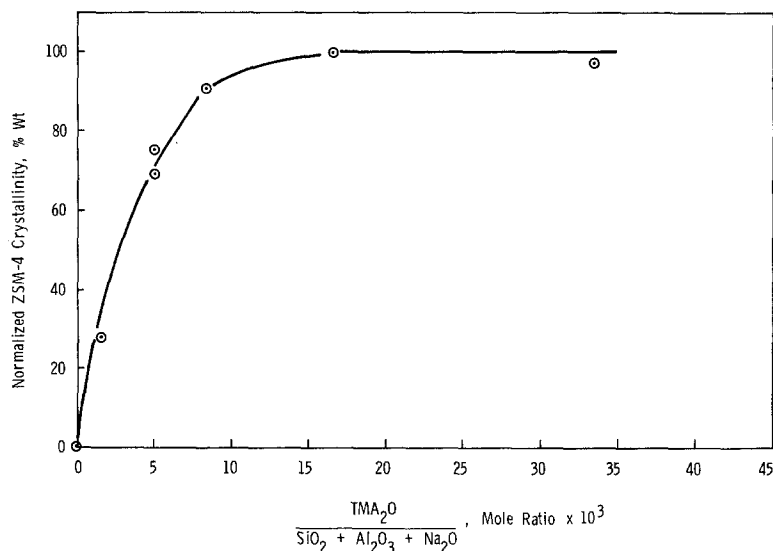


FIG. 1. Effect of TMA⁺ content of reaction mixture on ZSM-4 content of product.

mentioned, the metastable nature of faujasite in its transition to P zeolite is well-known but the transition to ZSM-4, facilitated by the tetramethylammonium ion (TMA), has not been previously reported. This work not only demonstrates this metamorphosis but gives a quantitative measure of the contribution of the TMA cation and, using scanning electron micrographs, gives some insight into the morphological change and the mechanism of recrystallization in going from faujasite to ZSM-4.

EXPERIMENTAL

Zeolite crystallization procedure. Zeolite crystallizations were performed utilizing the technique of Ciric and Reid (4) in which a "faujasite crystal directing," FCD, mixture is employed. The crystallizations were conducted by first forming the FCD mixture, aging for 0.5 hr at 60°C then combining with the remaining reactants to form an amorphous hydrogel. The hydrogel was then placed in polypropylene jars and put in a steam chest for static crystallizations, or in a thoroughly agitated, stream-jacketed five-gallon autoclave. The

progress of the crystallization was monitored by periodical sampling in such a manner as to not essentially disturb the crystallization conditions.

This procedure using the agitated autoclave was chosen to minimize mass and heat transfer gradients during crystallization that might exist in static crystallizations.

TABLE 1

Composition of Crystallization Reaction Mixtures

	Type of crystallization	
	Static	Agitated
FCD mixture (mole)		
SiO ₂	16.0	16.0
Al ₂ O ₃	1.0	1.0
Na ₂ O	29.4	29.5
H ₂ O	530.0	528.0
Total hydrogel		
SiO ₂	15.4	15.4
Al ₂ O ₃	1.0	1.0
Na ₂ O	6.6	6.5
TMA ₂ O	0 to 0.77	0 and 0.38
H ₂ O	487.0	487.0
Wt FCD/wt of total hydrogel	0.22	0.22

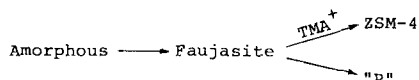
Reactant materials for zeolite synthesis. Sodium silicate (Q-Brand) was obtained from the Philadelphia Quartz Company, Ludox (LS) colloidal SiO_2 from the E. I. du Pont de Nemours Company, sodium aluminate from the Nalco Chemical Company, and TMACl from the R.S.A. Company. Also used were: NaOH, $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$, and H_2SO_4 .

Zeolite characterization. Crystallinity measurements were made using standard X-ray diffraction techniques with a Phillips diffractometer, Model 26 DNOA. SEM pictures were taken on a Joel Model 58 high resolution scanning electron microscope. Zeolite samples were washed, dried, and then redispersed in methanol before standard sample preparation.

RESULTS AND DISCUSSION

ZSM-4 Crystallization

The initial experiments in this study were static crystallizations. From these experiments the following reaction sequence was observed for the crystallizations:



The amounts of ZSM-4 and "P" formed when crystallization is complete are proportional to the concentration of TMA^+ in the reaction mixture (Fig. 1). It is clearly seen that above a certain TMA^+ concentration the reaction path to "P" can be eliminated yielding only ZSM-4.

These static crystallizations were conducted using the previously described procedure employing a "faujasite crystal directing," FCD, mixture at 100°C and autogeneous pressure. The FCD procedure was chosen over other static crystallization procedures because it most clearly delineates the mechanistic path to faujasite and subsequently to ZSM-4. The composition of the reactants is shown in Table 1.

Based upon the results of these initial experiments, a larger-scale crystallization was conducted using a thoroughly agitated five-gallon autoclave. As previously mentioned, the use of the agitated autoclave for crystallization was to minimize if not eliminate any mass and heat transfer gradients that might exist in the reaction mixture during crystallization. In addition, the frequency of sampling was increased to more quantitatively define the transition from amorphous through faujasite to ZSM-4. The formulation chosen for the agitated crystallization (Table 1) was one

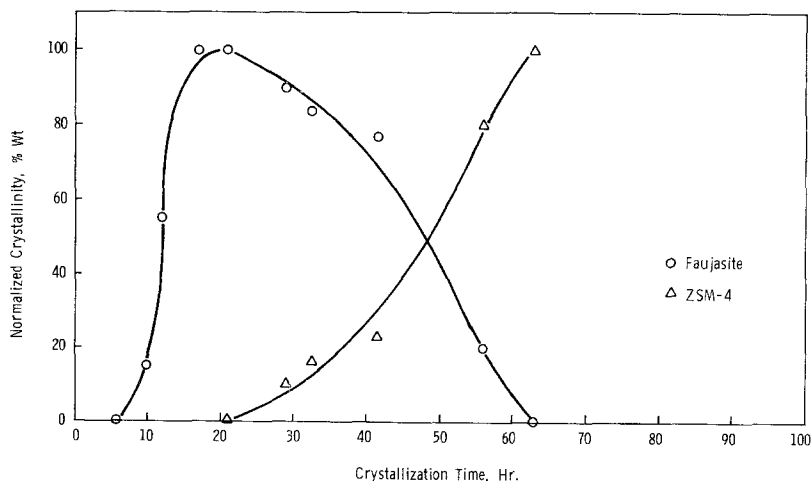


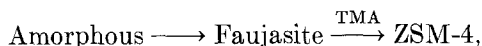
FIG. 2. Crystallinity as a function of time—autoclave crystallization.

TABLE 2
Composition of Pure Crystalline Products

	Zeolite type		
	Faujasite	ZSM-4	"P"
SiO ₂ (mole)	4.9	6.8	4.95
Al ₂ O ₃	1.0	1.0	1.0
Na ₂ O	0.98	0.80	0.90
TMA ₂ O	0.04	0.25	0.0

in which the formation of "P" zeolite was eliminated. As might have been expected, the total crystallization time for the larger-scale agitated crystallization was reduced from about 14 to 3 days indicating that mass transfer limitations did exist in the static crystallizations but did not have an effect on the reaction path.

The course of the crystallization was monitored by periodic sampling, and the crystallinity results are shown in Fig. 2. These results clearly substantiate the crystallization mechanism,



observed in the static crystallizations. There is no indication of a simultaneous or competitive crystallization since no ZSM-4 is formed until the faujasite crystallization is complete. Also there is no evidence to indicate that the faujasite reverts to an amorphous material which serves as a nutrient source for the recrystallization of ZSM-4. The data clearly indicate a distinct and orderly transition from faujasite to ZSM-4. Chemical analyses of the faujasite stage and final ZSM-4 product are presented in Table 2.

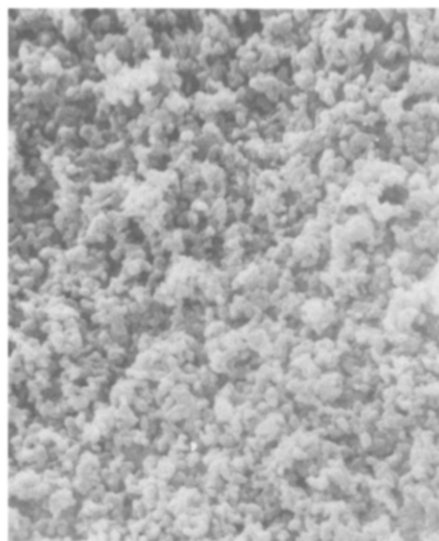
The mechanism of zeolite crystallization has been the subject of considerable research, and excellent review articles have been written by Zhdanov (5) and Flanigen (6). The two main mechanisms that have been proposed for zeolite crystallization have been from a "solid gel phase" or a "solution phase." In the

system under study, faujasite \rightarrow ZSM-4, the solid gel route can be eliminated because of the lack of appearance of a solid amorphous phase between the crystallization of faujasite and the appearance of ZSM-4. In order to determine whether a "solution phase" was the mechanism, the mother liquor was analyzed for SiO₂ and Al₂O₃ periodically during the agitated crystallization experiment. In a "solution phase mechanism," we might expect to see an increase in the Al₂O₃ and SiO₂ content of the mother liquor due to the dissolution of faujasite. The analyses shown in Table 3 do not show an increase in Al₂O₃ content. The variation in SiO₂ content is probably within experimental error. This does not negate the "solution phase" mechanism but indicates that the rate of solution of faujasite is either very slow or the rate of crystallization from solution to ZSM-4 is very rapid with the net result that there is no accumulation of Al₂O₃ and SiO₂ in the mother liquor.

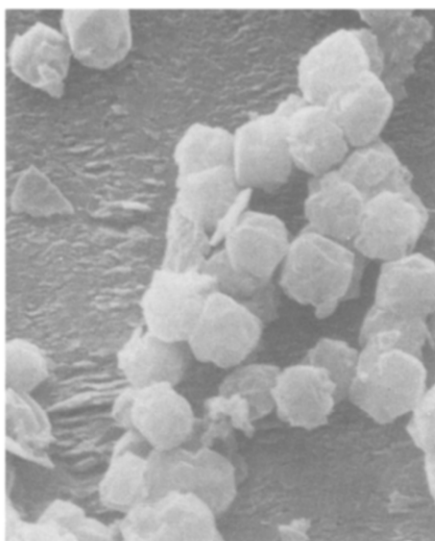
To further understand the mechanism of this morphological transition, scanning electron micrographs were taken of the same samples used for the crystallinity measurements and are shown in Figs. 3 and 4. From these pictures we can see the

TABLE 3
Mother Liquor Analyses for Amorphous \rightarrow
Faujasite \rightarrow ZSM-4

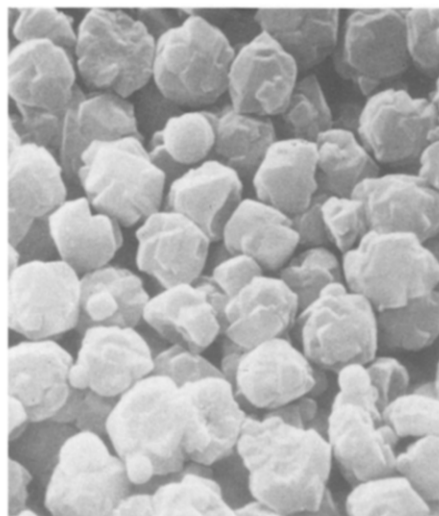
Crystallization time (hr)	Product composition	Mother liquor	
		SiO ₂ (wt%)	Al ₂ O ₃ (wt%)
2	Amorphous	6.15	0.01
6	Amorphous	6.15	—
10	15% Faujasite	6.39	—
12	55% Faujasite	6.38	0.01
17	100% Faujasite	6.28	—
32.5	84% Faujasite 16% ZSM-4	6.04	0.01
41.5	77% Faujasite 23% ZSM-4	6.83	—
63	100% ZSM-4	6.46	0.01



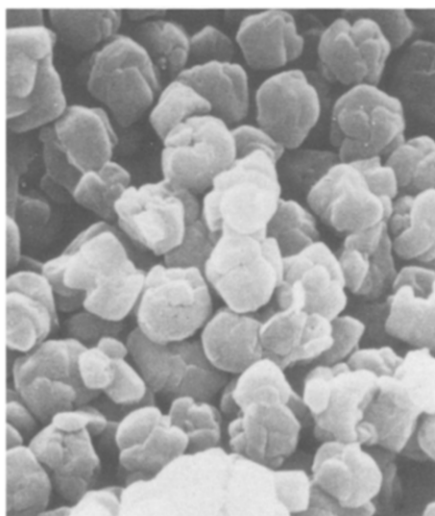
6 Hr.
AMORPHOUS



10 Hr.
15% FAUJASITE



17 Hr.
100% FAUJASITE

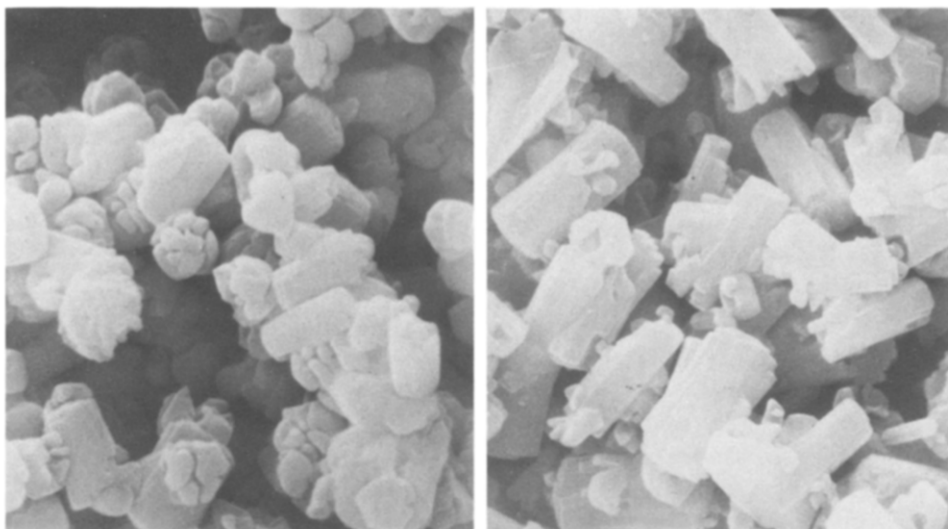


32.5 Hr.
84% FAUJASITE-16% ZSM-4

Fig. 3. Scanning electron micrographs (7700 \times) of faujasite-ZSM-4 metamorphosis.

formation of the octahedral faujasite crystals, their subsequent degradation, and the emergence of the hexagonal prismatic rods of ZSM-4. This ZSM-4 morphology is similar to that observed for (the ap-

parently isostructural mineral) Mazzite (hexagonal needles) (?). The faujasite samples, that are free of ZSM-4, are smooth-surfaced octahedral crystals with sharp, well-defined edges and corners.



41.5 Hr.
77% FAUJASITE-23% ZSM-4

56 Hr.
20% FAUJASITE-80% ZSM-4



63 Hr.
100% ZSM-4

Fig. 4. Scanning electron micrographs (7700 \times) of faujasite-ZSM-4 metamorphosis.

As ZSM-4 appears, the faujasite crystals show signs of erosion and the loss of their well-defined crystal morphology. The appearance of the hexagonal prismatic rods

of ZSM-4 attached to the surface of the faujasite crystals is also seen. As the ZSM-4 crystals become fully developed, defects in the crystal are seen corresponding

to the point of nucleation with the faujasite crystal precursor. These observations are consistent with a mechanism that would include a surface solution of the faujasite crystals to supply nutrient for the ZSM-4 crystallization which is nucleated by the surface of the same faujasite crystals.

Faujasite Crystallization

For the purpose of comparison a crystallization was carried out identical to the previously described ZSM-4 crystallization, only omitting the tetramethylammonium ion (TMA) in the formulation. In this case, as in the ZSM-4 crystallization, faujasite readily crystallized. As the crystallization proceeded, the faujasite degenerated and other crystalline phases appeared. The crystallization was continued until all traces of faujasite had disappeared and the concentration of the final crystalline form, which in this case was P zeolite, appeared stable. A similar experiment using a static crystallization also resulted in zeolite "P" as the final crystalline product.

The change in crystalline composition is shown in Fig. 5. Good quantitative measures of the amount of secondary crystalline material could not be made from

the X-ray diffraction patterns during the transitional stage in which there were mixtures of faujasite and the final crystalline phase. Chemical analyses of the faujasite phase and the final "P" zeolite phase are presented in Table 2.

SEM pictures of the products during the course of the crystallization were also taken corresponding to the crystallinity measurements (Fig. 6). Again we see the formation of the faujasite crystals, their subsequent degradation and the emergence of the "P" crystals. The final "P" crystals show some signs of defects which may be caused by nucleation sites from the faujasite, but they are not as dramatic as seen in the ZSM-4 metamorphosis.

SUMMARY

In this paper an experimental demonstration of crystalline metamorphosis in zeolite synthesis has been presented. The study has used faujasite as the metastable crystalline phase. The incorporation of tetramethylammonium ions does not just change the cation composition of the faujasite, but rather directs the crystallization mechanism to the more stable ZSM-4 phase. In addition, the secondary

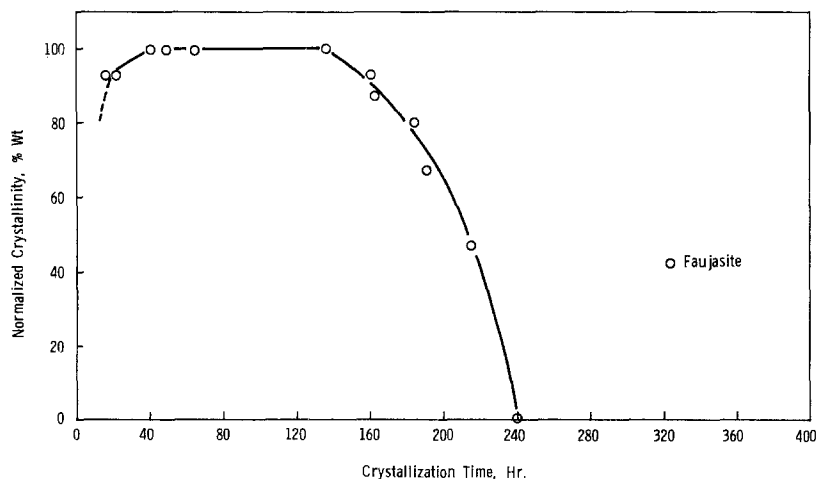


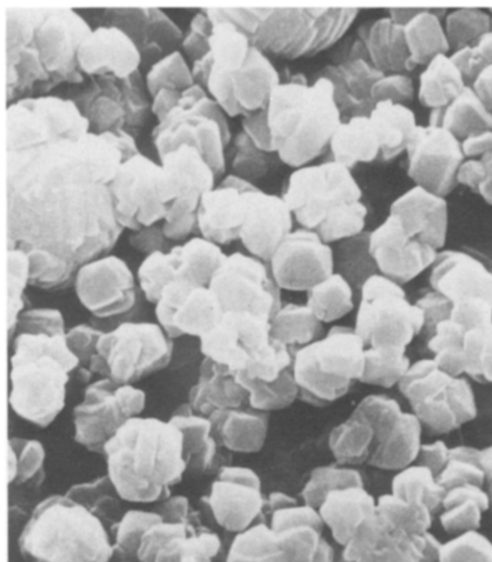
Fig. 5. Crystallinity as a function of time—autoclave crystallization.

crystallization appears to nucleate on the surface or edges of the faujasite crystal rather than from the mother liquor. This

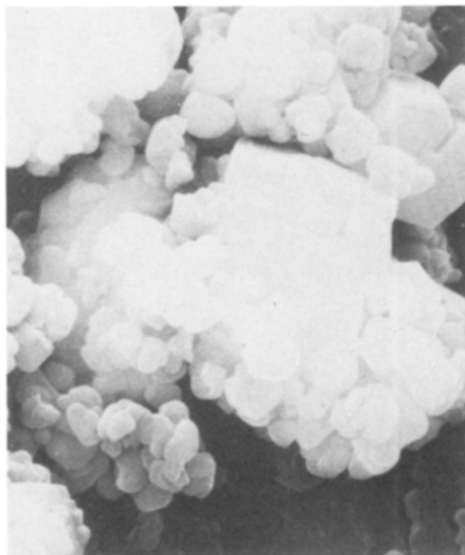
work extends the observations reported by Breck (1) that concentration changes in the reaction mixture can reduce the



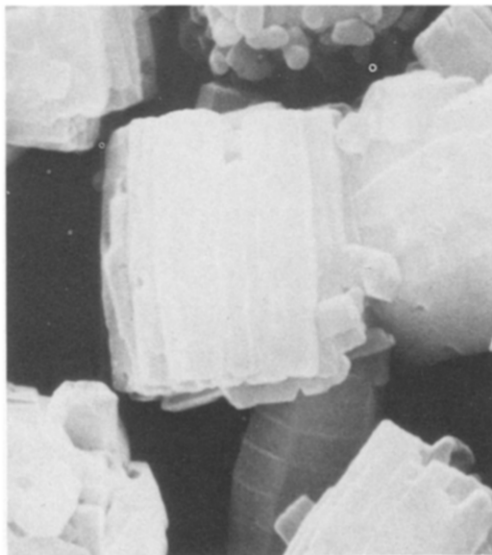
6 Hr.
AMORPHOUS



49 Hr.
100% FAUJASITE



185.5 Hr.
80% FAUJASITE



239 Hr.
100% Zeolite P

FIG. 6. Scanning electron micrographs (7700 X) of faujasite-"P" transition.

crystallization in that the change in direction is brought about by the addition of a new ion, TMA.

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