JOURNAL OF CATALYSIS **48**, 129–136 (1977)

Fluid Faujasite Particulates
Nucleation, Crystallization and Pseudomorphism

Bankim Dhanak and L. B. Sand

Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, Massachusetts 01609

Received October 29, 1976; revised February 26, 1977

This paper reports on crystallization phenomena observed in a new technique of direct synthesis of particulates in the fluid cracking catalyst size range of faujasite-type zeolite molecular sieve. The procedure, using sized sodium aluminate particles reacting with salt-containing sodium silicate solutions, produces zeolite particulates pseudomorphic after intermediate gel particles. Promoting rapid, uniform growth of small (0.2 μm) intergrown octahedra crystals from numerous nuclei results in pseudomorphic particulates which are attrition-resistant.

INTRODUCTION

This paper reports on the results of a study to form strong molecular zieve zeolite crystal aggregates in the fluid size range by direct synthesis techniques. Although the technique also applies to other zeolites, the results on synthetic faujasite are reported first because of its large volume use in fluidized processes. Fluidized particles usually are prepared from separate syntheses of silica–alumina gel and of zeolite, and spray drying the zeolite-containing (10–25%) gel slurry to the desired size range. The particulates described in this paper are of interest for use in chemical processes in which strong fluid particulates with a high zeolite content to 100% are preferred.

Although the synthetic faujasite-type zeolites are the most important molecular sieve zeolites currently used, relatively little quantitative data on the mechanism and kinetics of nucleation, crystallization and resulting morphology have been reported as can be seen in the comprehensive review by Breck (*1*). The growth of individual crystals, not the growth of crystal aggregates within particles, were of interest in the scientific studies reported in the literature. Patent literature describing the preparation of "binderless" or "self-bonded" zeolite crystal aggregates by *in situ* reaction is reviewed by Breck (*1*).

The fundamental objective of this study was to determine the mechanisms involved in the growth of zeolite crystal aggregates in particulates formed during pseudomorphic conversion. This term is used in the broad sense to describe the process of *in situ* replacement of one species by another while retaining the size and shape of the original.

METHODS

After a series of exploratory runs, using conditions for crystallization of faujasite-type zeolite X reported in the literature (*2*), a batch composition $8.2Na_2O–Al_2O_3–11.4SiO_2–147.74H_2O$ with numerous salt additions per mole of Al_2O_3 was selected for the study. Salts were added to the system from a working hypothesis that in-

ISSN 0021-9517

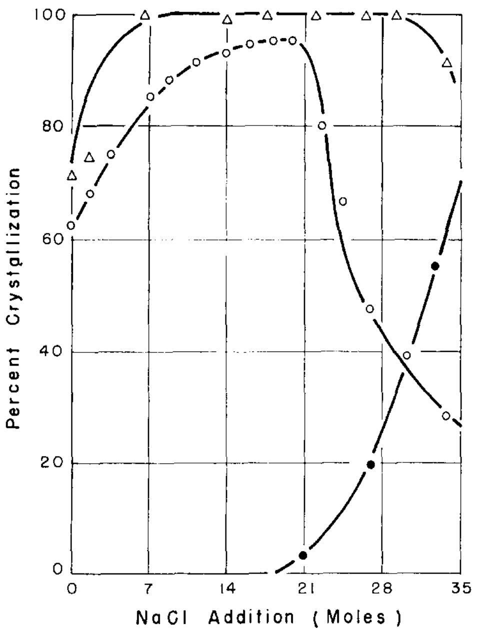


FIG. 1. Effect of NaCl addition on extent of crystallization after 6 hr at 100°C. (△) Faujasite-type, stirred system; (○) faujasite-type and (●) zeolite B, unstirred system.

creased viscosity and physical separation of the precursor particles would promote pseudomorphic conversion. Reactants used were sodium aluminate particles of appropriate size distribution range (Nalco, $1.1Na_2O$–Al_2O_3–$3H_2O$), sodium silicate solution ("N", Philadelphia Quartz, $0.3Na_2O$–SiO_2–$7.3H_2O$), sodium hydroxide (Mallinckrodt, analytical reagent) and distilled water. Additions to this base starting mixture were sodium chloride (Mallinckrodt, USP) and sodium bromide (Mallinckrodt, USP, analytical reagent). Gel aggregates in the size range of fluidized cracking catalyst formed from appropriate combinations of these reagents. The batch formulations were autoclaved in 15 ml capacity 314 low carbon stainless steel reactor vessels with Teflon seals. The sealed autoclaves were placed in ovens at temperatures in the range 80 to 150°C after an induction period of 16 hr at 25°C. On completion of a run, the autoclave was quenched, the contents were extracted and

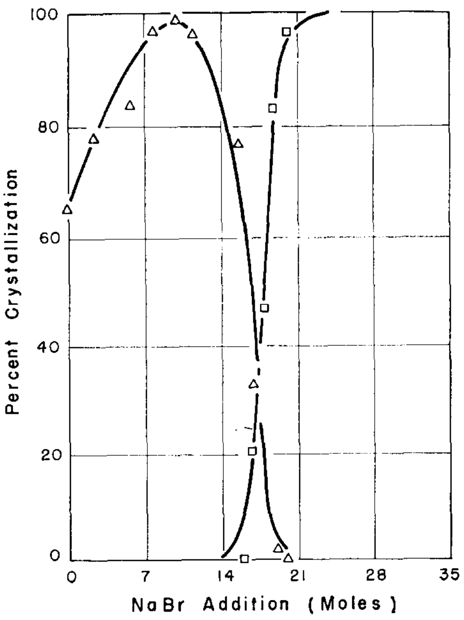


FIG. 2. Effect of NaBr addition on extent of crystallization after 6 hr at 100°C. (△) Faujasite-type, (□) zeolite HS (hydroxysodalite).

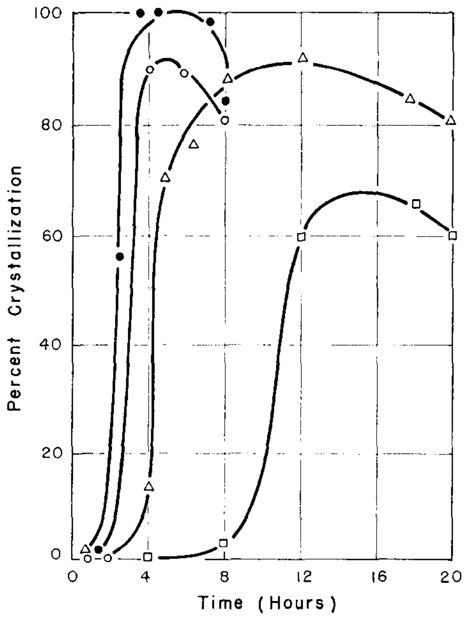
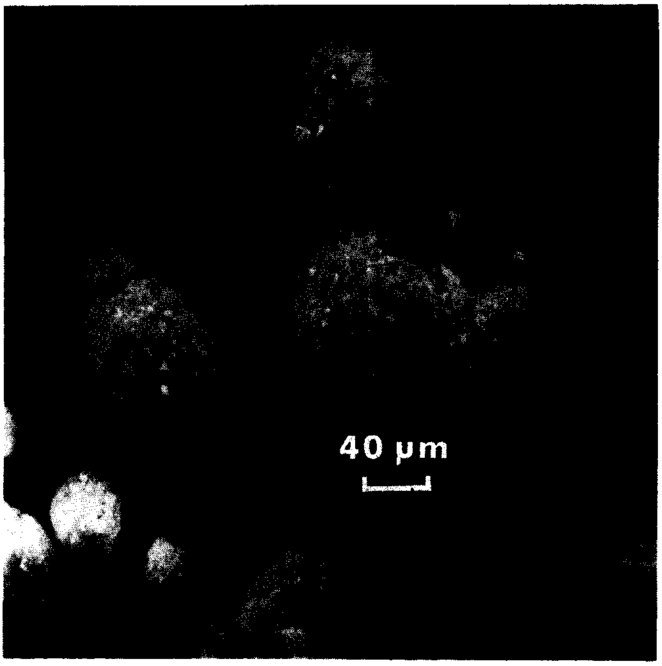


FIG. 3. Crystallization curves at (□) 80°C, (△) 100°C, (○) 120°C and (●) 130°C with 6NaCl for addition.



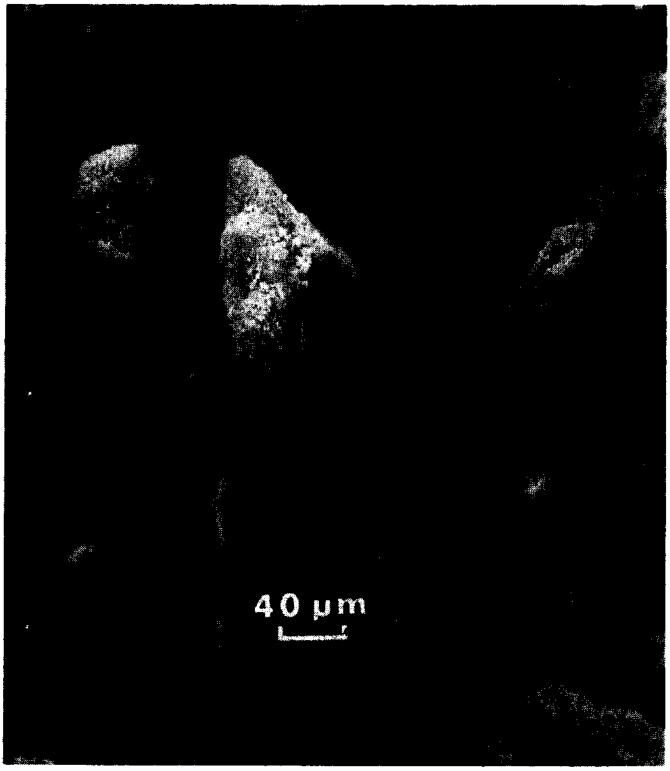


Fig. 4. (Top) gel particles pseudomorphic after sodium aluminate particles. 8NaCl addition. (Bottom) faujasite-type particulates pseudomorphic after the gel particles seen in (top).

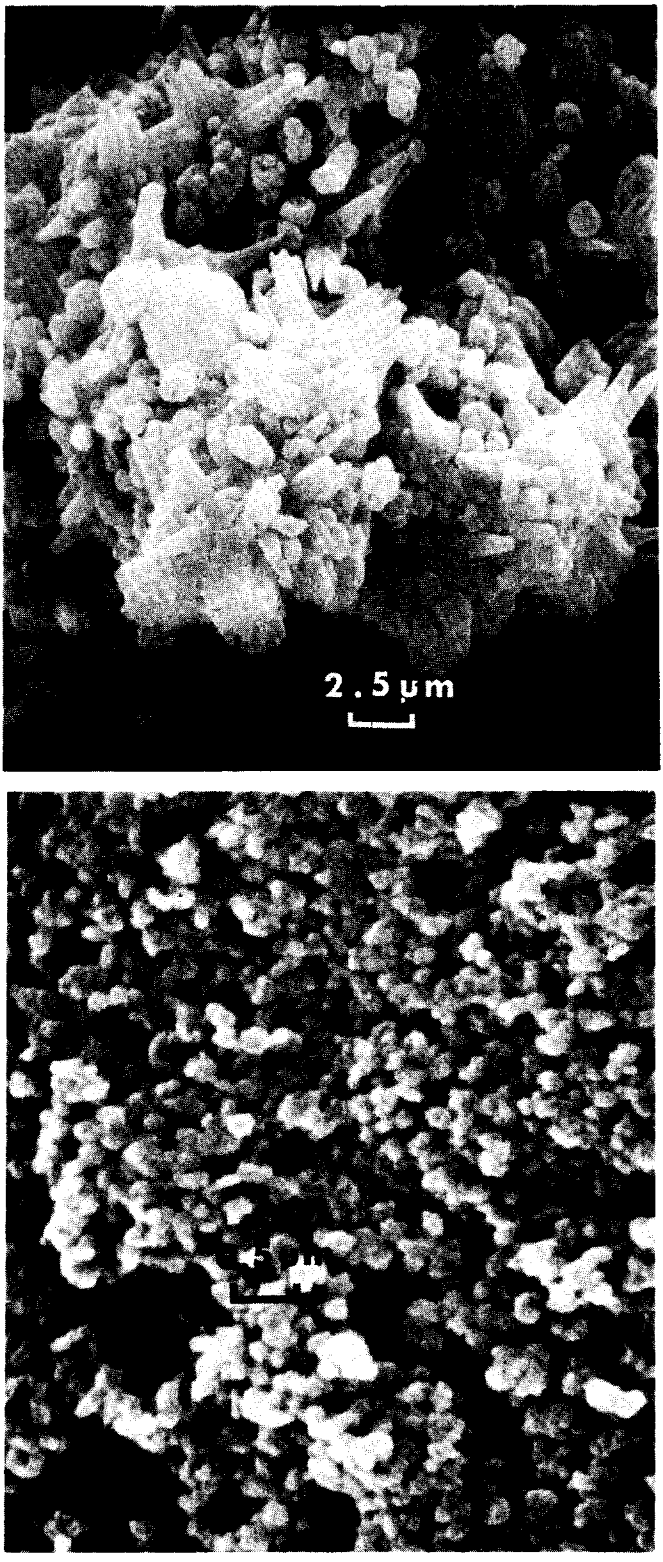


FIG. 5. (Top) skeletal faujasite-type crystals formed in the 8NaCl addition system at the 67% crystallization stage. (Bottom) individual crystals (0.2 μm) of faujasite-type particulates shown in Fig. 4 (bottom).

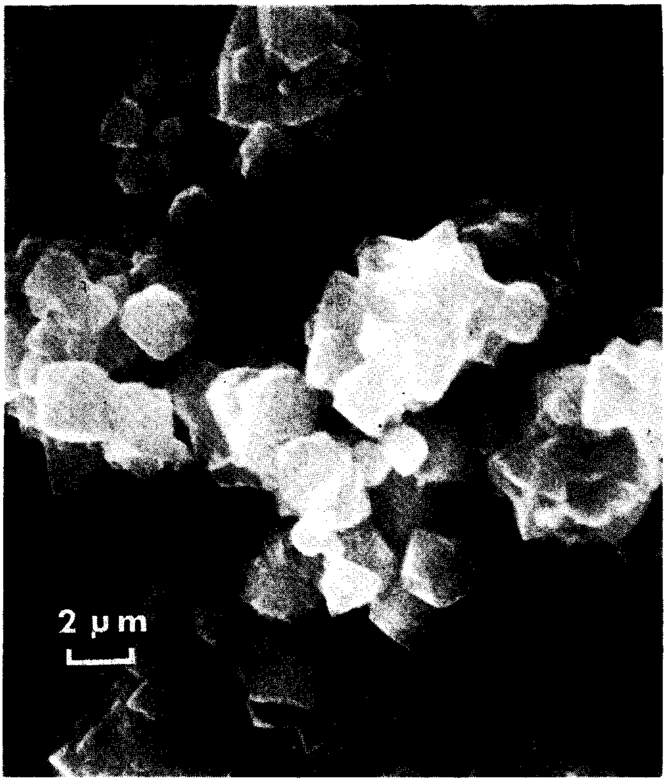


FIG. 6. Twinned octahedra crystals (1.7–2.0 μm) of faujasite-type in particulates formed in the 6NaBr addition system.

mulled gently before filtering with water wash on a Buchner funnel to pH 8.

Crystallization curves were obtained by the method of peak summation from X-ray powder diffraction patterns using standard reference samples. The curves were obtained at three temperatures (80, 100, 120°C). Rates of conversion were obtained by taking slopes at 50% conversion and used for the Arrhenius plot. Scanning electron micrographs were obtained using a Jelco Model U3 on samples made conductive with a Au–Pd evaporated film. Size distribution curves were obtained on a Sharples micromerograph. The attrition resistance test consisted of running 50 mg of the particulates for 6 min in a Spex Industries Wig-L-Bug. Comparative sorption rate curves were obtained on a Keisling adsorption balance (*3*).

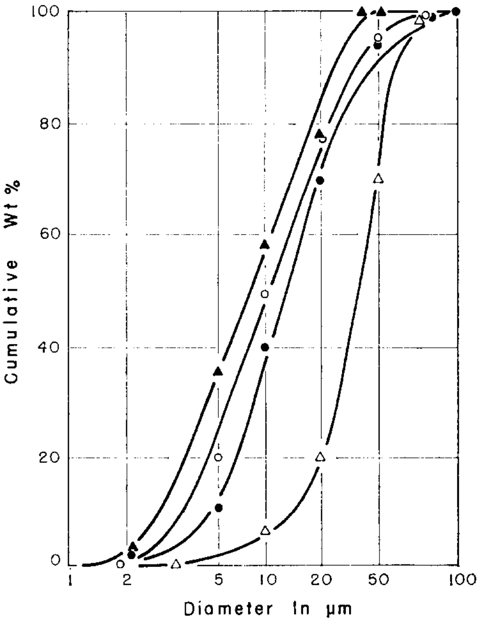
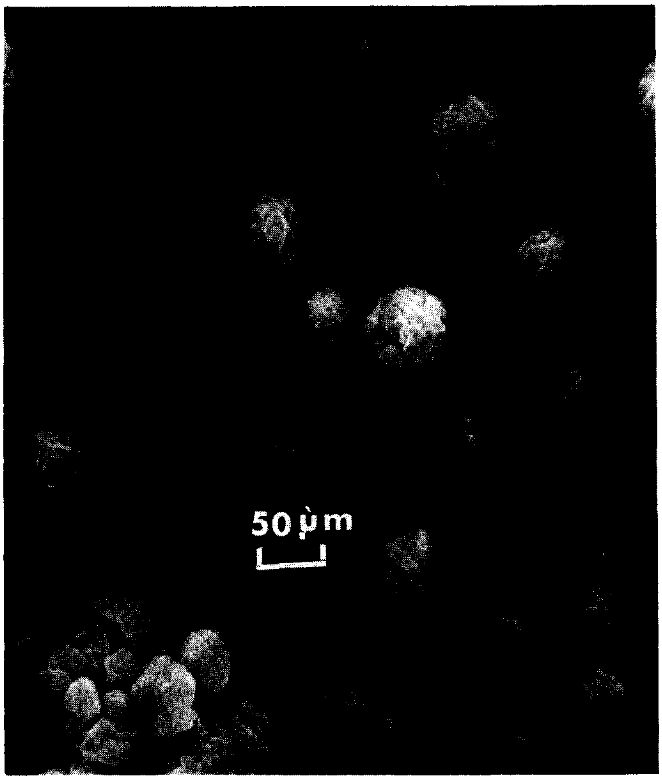


FIG. 7. Particle size analysis of cracking catalyst and faujasite-type particulates before and after attrition test. (△) Cracking catalyst before, (▲) cracking catalyst after, (○) zeolite X particulates before, (●) zeolite X particulates after.

RESULTS

Faujasite-type crystal aggregates also were obtained in systems with no salt addi-



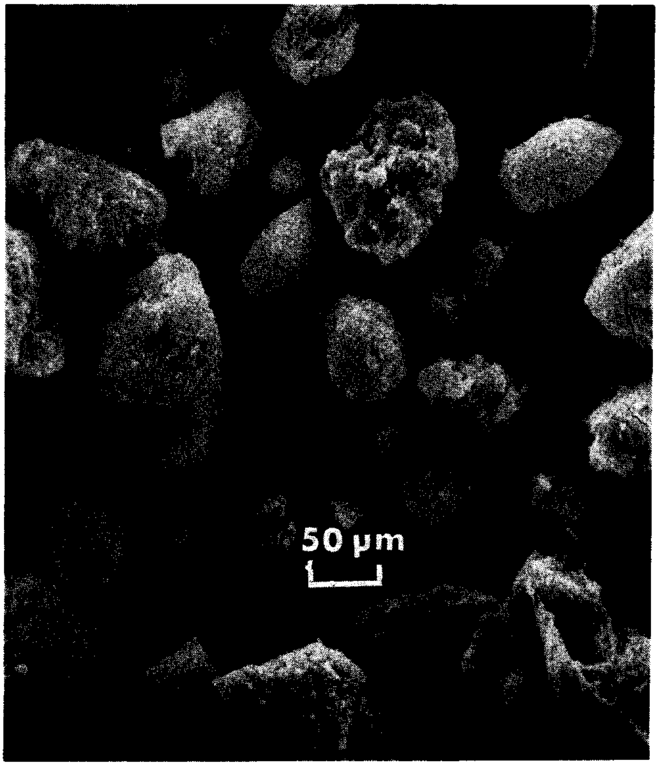


FIG. 8. (Top) fluidized cracking catalyst after attrition test; (bottom) faujasite-type particulates after attrition test.

tions and with other salts, but only typical data obtained from one batch composition with either NaCl or NaBr addition are included in this paper.

The correlation between NaCl addition and resulting crystallization curves is shown in Fig. 1; a similar correlation with NaBr additions is shown in Fig. 2. The addition of the salts affected both percentage crystallization and crystal size in the aggregates. Salt additions up to 34 moles and autoclaving times up to 250 hr still produced faujasite as a metastable phase. Figure 3 shows the kinetics of crystallization as a function of temperature in one subsystem (6NaBr addition). An Arrhenius plot taken from these data gave an apparent activation energy for crystallization of 17.2 kcal gmole^{-1} (*4*).

Figure 4 (top) is a scanning electron photomicrograph showing the pseudomorphic replacement of the sodium aluminate particle by gel; Fig. 4 (bottom) shows the final faujasite-type crystal aggregate particulate pseudomorphic after the gel particle. The skeletal octahedra shown in Fig. 5 (top) were obtained in the 9NaCl system after 6 hr and illustrates an intermediate stage of development of the intergrown crystal aggregates during rapid crystal growth. Figure 5 (bottom) is typical of the surface of the crystal aggregates showing individual crystals 0.2 μm in size. Well-formed octahedra result in some systems which is illustrated in Fig. 6—a scanning electron photomicrograph taken of the surface of a particulate formed in the 6NaBr addition system after 10 hr at 100°C. The individual crystals measure 1.7–2.0 μm.

In Fig. 7 are given the size distribution curves before and after the attrition test for faujasite-type particulates prepared in the 10NaCl system at 100°C for 17 hr as compared with a zeolite-containing fluidized cracking catalyst. Figure 8 shows SEM's of the cracking catalyst (top) and zeolite particulates (bottom) after being subjected to the attrition test.

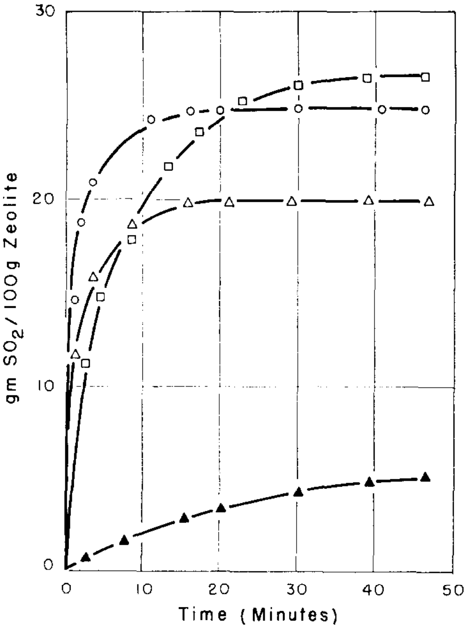


FIG. 9. Sorption curves for SO_2 at 25°C and 70 mm Hg. (○) 13X powder, (▲) faujasite-containing cracking catalyst, (□) faujasite-containing cracking catalyst normalized, (△) faujasite-type particulates (containing 85% zeolite) of this study.

In Fig. 9 are given comparative sorption rate curves for particulates containing 85% faujasite-type crystals obtained in this study, for the zeolite-containing fluidized cracking catalyst, and for 13X polycrystalline powder.

Additional results in other systems and subsystems are given by Dhanak (*4*).

DISCUSSION

Particulation of synthetic molecular sieve zeolites may be regarded as one of the more difficult areas of zeolite technology, and relatively little data are published in the scientific literature. The particulates generally are formed with the addition of a gel or clay binder using the forming techniques of prilling, spray drying (*5*), pelletizing, rolling and extrusion. Most closely related to the work reported in this paper is the fabrication of "self-bonded" or "binderless" particulates by preforming reactants, representing a partial batch composition, calci-

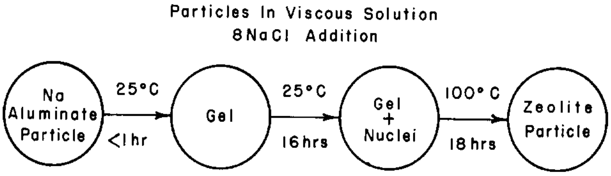


FIG. 10. Proposed model of sequence of pseudomorphic transitions in an unstirred system.

nation to provide dry green strength, and reaction in water, vapor, or a solution to crystallize the zeolite while retaining the shape of the particulate. In the preparation technique of this study the parent gel particulates are formed directly from the complete batch composition by selection of reactant particles which react with solution to finally form zeolite crystal aggregate particulates pseudomorphic after intermediate gel particles. The sequence is diagrammed in Fig. 10. Contrasted to the slaking problem inherent in the other techniques, these final particulates are stable in appropriate aqueous solutions for ion exchange, either for preparing catalysts or adsorbents, or for use as an ion exchanger. Another principal advantage of this method is the ability to obtain better than 90% zeolite in fluid particulates. The particulates are attrition-resistant as there was no significant change in particle size distribution noted from the attrition test as compared to a commercial cracking catalyst.

This unique phenomenon of formation of pseudomorphic zeolite aggregate particulates after intermediate gel particles is explained as follows. The method produces gel particles which contain all the nutrients necessary for nucleation and crystallization and can be regarded as individual synthesis systems within the reactor vessel. Supporting this hypothesis is the similar nucleation and crystallization rates when increased salt additions disperse the gel particles. No changes, such as diffusion limitations, slower nucleation rates, or crystallization as a function of time, which one would expect in a mass transfer limited system, were observed. There are four stages in the reaction system: first, the precursor aluminate particles react to form pseudomorphic gel particles which then act as individual reaction subsystems; second, the initial nuclei of faujasite are formed at ambient temperature; third, after a higher temperature–time period which is independent of salt content, the numerous nuclei grow rapidly at the same rate, resulting in intergrown crystals of the same size; in the final stage a slower but uniform growth rate of all crystals occurs as the nutrient is depleted. The usual phenomenon of larger crystals growing at the expense of the smaller crystals with higher surface energy does not occur. Thus, the uniform growth without dissolution results in an intergrown crystal aggregate particulate which retains the morphology of the precursor particles.

ACKNOWLEDGMENTS

Partial financial support from the Department of Chemical Engineering, WPI, is gratefully acknowledged. Size distribution curves were obtained through the courtesy of Dr. R. Hight. Professor R. Biederman and Mr. G. Schmidt provided the facilities and assistance in taking the SEM's.

REFERENCES

1. Breck, D. W., "Zeolite Molecular Sieves", Wiley, New York, 1974.

2. Milton, R. M., *U. S. Pat.* 2,882,244, Apr. 14, 1959.

3. Keisling, C. A., Hayhurst, D. T., and Sand, L. B., *Fundam.*, in press.

4. Dhanak, B., MS thesis, Dept. of Chem. Eng., Worcester Polytechnic Inst., 1975.

5. McDaniel, C. V., and Maher, P. K., *U. S. Pat.* 3,472,617, Oct. 14, 1969.