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CRYSTALLIZATION OF LARGE CRYSTAL SILICALITE IN THE SYSTEM WITHOUT HYDROXIDE ADDITION

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Reactant mixtures with salts as the only source of alkali metal were prepared for hydrothermal synthesis of silicalite. Crystals of size well above 100 μm were identified in some experimental runs. A simple relationship between the crystal size and the amount of added salt was established.

The objective of this research was to study the crystallization of silicalite in a system with salts as only source of alkali cations in the reaction mixture. The work identified a range of reactant compositions which would yield large zeolite crystals.

Synthesis of the pentasil zeolite, ZSM-5, and its end member product silicalite has been the topic of several investigations.[1-5] Typical oxide formula of the starting reactant mixtures is aNa_2O-bAl_2O_3-$cSiO_2$-dTPABr-eH_2O where a,b,c,d and e can be varied over a range of compositions. In this reacting mixture, the organic templating agent tetrapropylammonium (TPA) ions are considered as structure directing species which aid in the arrangement of the tetrahedra units. A base function is usually added which has the purpose of dissolving reactant gels to form active phase. This is the first step in zeolite crystallization. The source of alkalinity in these reaction mixtures is commonly a strong base such as NaOH.

Chao and co-workers,[6] however, found that ZSM-5 will crystallize in a system without TPA ions. Nakamoto and Takahashi[7] reported a reaction mixture with TPA single cation in the ZSM-5 synthesis. Mostowicz and Sand,[8] used sodium salts as the only source of alkali metal in ZSM-5 crystallization. The use of

other organic templates in place of the TPA ions has also been reported.[9,10] In most of these investigations, pentasils were found to be aggregates of fine crystals at the size of few microns in length. Von Balmoos et al. [11,12] have reported the growth of large ZSM-5 crystals although yields of these large crystals were limited. In this laboratory, we have successfully crystallized silicalite crystals well above 200 μm in length from traditional Na_2O-TPABr-SiO_2-H_2O system. Here we want to report the synthesis of large silicalite crystals from a system with salts as the only source of alkali metal.

The reactant materials used were Ludox-AS40 (du Pont), tetrapropylammonium bromide (Aldrich Chemical, 98%), sodium citrate (Fisher Scientific, certified grade, >99.5%), ethylenedinitrilo tetraacetic acid tetrasodium salt (MCB, 99%) and sodium chloride (MCB, reagent grade). Reactants were mixed to form mixtures with the composition shown in Table 1. Synthesis were carried out in Teflon-lined autoclaves of 15 ml capacity at 185°C under autogeneous pressure for one week. Products were filtered and washed five times with distilled water. The filtered cakes were boiled with 50% sodium hydroxide solution to remove unreacted gels. Zeolite crystals were washed with distilled water five times before being characterized. Optical microscope was used for a preliminary screening of crystal size and scanning electronic microscope (SEM) was used for a quantitative size identification.

Results from this research program are summarized in Table 1 where the reactant mixture composition and resulting crystal size are listed. In Fig. 1 a linear relationship between the product's crystal size and the amount of salts added in the reactant mixtures is shown. In the specific concentration range studied, larger crystals were obtained from mixtures with higher sodium content. This is a surprising result, as the sodium ions had been considered to have a structure-forming effect in pentasil synthesis,[13] and therefore higher concentration of Na cations in the reactant mixture are considered to facilitate rapid nucleation. Consequently, the number of nuclei formed would be large and many small crystals would be formed. The results shown in Fig. 1 do not support this expectation. The observations indicate that the anions may also have a strong inhibitive effect on the nucleation.

Figure 2 shows the scanning electromicrograph of the silicalite crystals obtained from Run #3. Uniform crystals of 180 μm in length were obtained from this batch composition. Some intergrowth of crystals could be observed along with

some penetration twinning of the silicalite. A small amount of unreacted materials were observed under, however, this second phase was found to be amorphous as x-ray diffractograms of the sample contain only peaks ascribable to silicalite. The amount of amorphous in each run was not quantified.

Products from each experimental run show uniformity in size except for silicalite crystallized from NaCl solutions. In the NaCl system a distribution of crystal sizes were observed. Most crystals were found to be smaller than 20 microns, however, a trace amount of large crystals were observed. This indicates that in the NaCl system the crystallization process resembles the type B mechamism as proposed by Derouane et al.[14] When Na- citrate or $(Na)_4EDTA$ is used as the cation source type A crystallization probably prevails.

In conclusion, results obtained from this research indicate that it is not necessary to add a strong base to the reacting solution to obtain large silicalite crystals. In addition, we have found that large silicalite crystals can be produced using different sodium salts in the reacting mixture and surprisingly, higher salt concentrations lead to crystals of larger size.

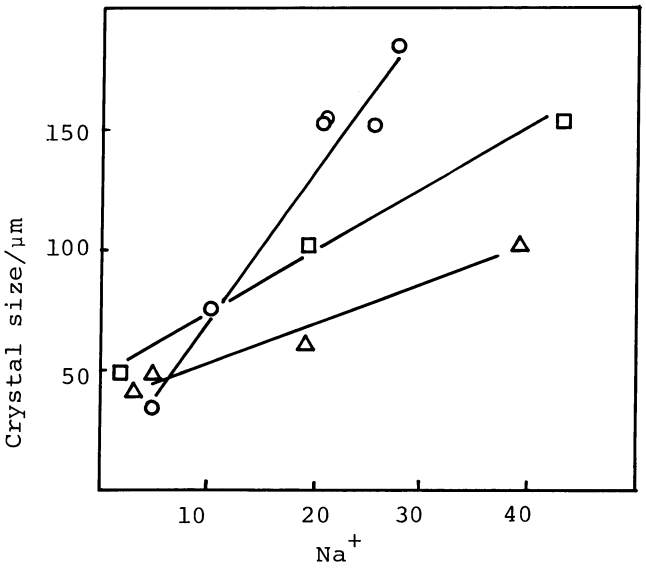

Fig. 1. Effect of Sodium Content on Crystal Size (□ NaCl, △ Na_4(EDTA), ○ Na citrate).

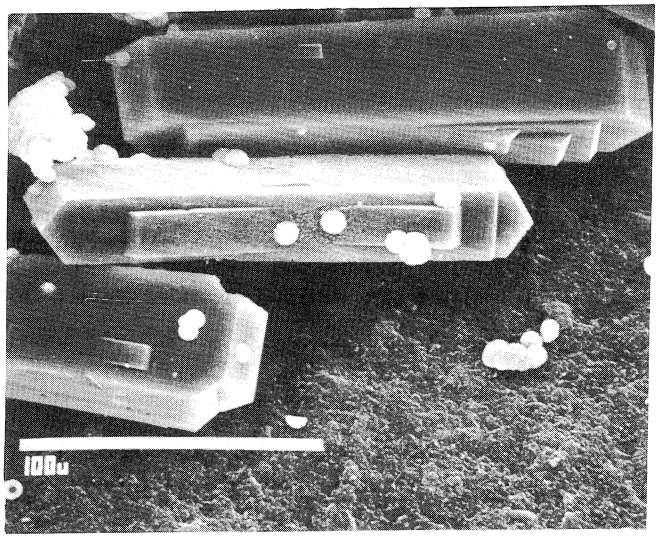

Fig. 2. Scanning Electronmicrograph of Silicalite.

Table 1. Reactant Compositions for Each Product

Run	Salts	Na/SiO_2	TPA/SiO_2	H_2O/SiO_2	Size μm
1	Na citrate	0.21	0.054	27.87	150
2	"	0.25	0.058	27.97	150
3	"	0.27	0.057	27.94	180
4	"	0.05	0.057	27.05	35
5	"	0.21	0.055	27.98	150
6	"	0.10	0.055	27.66	70
7	Na_4(EDTA)	0.39	0.056	28.08	100
8	"	0.03	0.055	28.50	40
9	"	0.05	0.054	27.89	50
10	"	0.19	0.057	28.44	60
11	NaCl	0.44	0.055	27.73	10-150
12	"	0.19	0.054	27.85	10-100
13	"	0.02	0.054	26.72	10-50

References

1) R.J. Argauer and G.R. Landolt, U.S. Patent 3702886 (1972).

2) D.M. Bibby, N.B. Milestone, and L.P. Aldrige, Nature, 285, 30 (1980).

3) R. Mostowicz and L.B. Sand, Zeolites, 2, 143 (1982).

4) E.M. Flanigen, J.M. Bennett, R.W. Grose, J.P. Chohen, R.L. Patton, and R.M. Kirchner, Nature, 271, 512 (1978).

5) A. Erdem and L.B. Sand, J. Catal., 60, 241 (1979).

6) K.Y. Chao, T.C. Tasi, M.S. Chen, and I. Wang, J. Chem. Soc., Faraday Trans. 1., 77, 547 (1981).

7) H. Nakamoto and H. Takahashi, Chem. Lett., 1981, 1739.

8) R. Mostowicz and L.B. Sand, Zeolites, 3, 219 (1983).

9) H. Nakamoto and H. Takahashi, Chem. Lett., 1981, 169.

10) H. Hagiwara, Y. Kiyozumi, M. Kurita, T. Sato, H. Shimada, K. Suzuki, S. Shin, A. Nishijima, and N. Todo, Chem. Lett., 1981, 1653.

11) R. von Ballmoos and W.M. Meier, Nature, 289, 782 (1981).

12) R. von Ballmoos, R. Busber, and W.M.Meier, Proc. 6th Iner. Zeolite Conf., 803, (1983).

13) E.G. Derouane, J.B. Nagy, Z. Gabelica, and N. Blom, Zeolites, 2, 299 (1982).

14) E.G. Derouane, S. Detremmerie, Z. Gabelica, and N. Blom, Applied Catalysis, 1, 201 (1981).

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