Simultaneous Crystallization of Two Dissimilar Zeolites from the System Ethylenediamine–Na_2O–Al_2O_3–SiO_2–H_2O–Triethylamine

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The zeolite ZSM-5 crystallizes in the solid gel phase and zeolite ZSM-35 crystallizes in the liquid phase of the system ethylenediamine–Na_2O–Al_2O_3–SiO_2–H_2O–triethylamine.

There are three current hypotheses on the mechanism of zeolite crystallization. Breck and Flanigen have argued that crystallization occurs in the solid phase,[1] and Kerr has proposed a mechanism of solution ion transport;[2] Gabelica and co-workers suggested that these two hypotheses can occur simultaneously.[3] Wenyang Xu and co-workers have reported that aluminate and silicate anions can not be determined from an organic solvent in the synthesis of mordenite in a non-aqueous system.[4] This paper reports for the first time the formation of ZSM-5 in the solid phase and ZSM-35 in the liquid phase in the presence of a specific amount of water.

The compositions of the liquid and solid phases are as follows: liquid phase: 1.0 ethylenediamine (EDA), 4.2 triethylamine, 15.1 water; solid phase: 4.0 Na_2O, 1.0 Al_2O_3, 70.2 SiO_2. The solid phase was packed into the cone portion of an acid-proof filter funnel (0.6—1.5 μm sieve diam.). The bottom of the funnel was sealed by sintering, then the funnel was put into a Teflon-lined autoclave. Water and alkylamine were put into the autoclave until the funnel was submerged (see Figure 1). The reaction was carried out at 150—200 °C. On crystallization, the products were deposited on the outside of the funnel or sieve plate (liquid phase product) and at the cone

Table 1. Typical reaction results.

	Reaction conditions		Products		SiO_2/Al_2O_3		LPW/SPW[c]
Run	$T/°C$	t/d	LP[a]	SP[b]	LP	SP	
1	150	3	—	10% ZSM-5	—	70.2	0.0
2	150	3	ZSM-35	ZSM-5	35.6	59.1	0.15
	200	3					

[a] Liquid phase product. [b] Solid phase product. [c] Weight (liquid phase product)/weight (solid phase product).

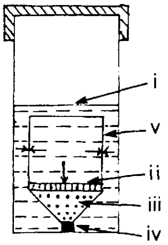

Figure 1. Sketch of reaction autoclave: i, liquid phase; ii, sieve plate; iii, solid gel phase; iv, sealed position; v, funnel outside (arrowheads indicate the area where liquid phase product is formed).

portion of the funnel (solid phase product). The products were washed and dried at 105 °C, then characterized by XRD and chemical analysis. Typical results are listed in Table 1.

In another experiment, the compositions of the liquid and solid phases were liquid phase: 1.0 ethylenediamine, 4.2 triethylamine; solid phase: 4.0 Na_2O, 1.0 Al_2O_3, 70.2 SiO_2. After the crystallization, only one product, ZSM-5, was obtained at the cone portion of the funnel; there were no products on the outside of the funnel and aluminosilicate anions were not determined in the liquid phase during the crystallization, indicating that crystallization occurs in solid phase.

It is clear from these two experiments that when a specific amount of water is added to the organic solvents, the silicate and aluminate anions can be determined in the liquid phase. The product of the solid phase is ZSM-5 and that of the liquid phase is ZSM-35 (weight ratio ZSM-35 : ZSM-5 = 0.15, Table 1). This indicates that zeolite is formed at a higher rate in the solid phase than in the liquid phase, a characteristic of the mechanism of solid phase transformation.

We propose that amorphous gels of the solid phase continuously dissolve and transport through the sieve plate to the upper side of the funnel, then nucleate and crystallize. A portion of the amorphous gels subsequently dissolves and aluminosilicate anions transport to the liquid phase, and so the crystallization carries on. At the same time, the aluminosilicate gels of the solid phase nucleate, crystallize and form ZSM-5.

These interesting phenomena have been observed for the first time in the synthesis of zeolites and support the hypothesis that solid phase transformation and solution ion transport can occur simultaneously. Certainly, the action of water could not be neglected.

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References

1 D. W. Breck and E. M. Flanigen, 137th meeting of the American Chemical Society, Division of Inorganic Chemistry, Cleveland, Ohio, 1960, p. 33.
2 G. I. Kerr, *J. Phys. Chem.*, 1966, 1047.
3 Z. Gabelica, N. Blom, and E. G. Derouane, *Appl. Catal.*, 1983, 227.
4 Wenyang Xu, Tao Do, and Shizheng Liu, CN 88, 100, 228.