

## **SOME NEW CONTRIBUTIONS TO UNDERSTANDING (OR MISUNDERSTANDING) OF MECHANISM OF CRYSTALLIZATION OF ZEOLITE ZSM-5 IN HETEROGENEOUS SYSTEMS (HYDROGELS)**

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### **ABSTRACT**

Changes of structural and particulate properties of the solid phase of the diluted reaction mixture were determined by X-ray diffraction (XRD), scanning-electron microscopy (SEM) and transmission-electron microscopy (TEM) and the concentration of silicon in the liquid phase was measured by atomic absorption spectroscopy. Based on the analysis of experimental results in accordance with known new-established postulation, a model of crystallization process is proposed.

Keywords: model of crystallization, zeolite ZSM-5, crystal growth, agglomeration

### **INTRODUCTION**

Although zeolite ZSM-5 was discovered almost 40 years ago [1], and although many fundamental principles of crystallization of MFI-type zeolites (ZSM-5, silicalite-1) were established during investigation of their crystallization processes in heterogeneous systems [2-6] and later confirmed by studying of the crystallization of MFIs (mainly silicalite-1) from initially clear solutions (homogeneous systems) [10], however the knowledge on the processes which occur at molecular level during crystallization of MFIs, and especially zeolite ZSM-5, is still in the stage of infancy. Thus, starting from the well established fundamental principles which are common for homogeneous and heterogeneous systems, each new contribution in the understanding of the critical processes (nucleation, crystal growth) of zeolite ZSM-5 crystallization has a great importance in the control of the chemical and particulate properties of the product of crystallization (zeolite ZSM-5) needed for specific its application(s). For this reason, we investigated structural and particulate changes of the solid phase during crystallization of zeolite ZSM-5 from diluted system, which can be assumed as a transition state between homogeneous (clear solution) and heterogeneous (dense hydrogel) systems.

### **EXPERIMENTAL**

The hydrogel having the batch molar composition:  $12.5\text{Na}_2\text{O}-8\text{TPABr}-\text{Al}_2\text{O}_3-60\text{SiO}_2-4000\text{H}_2\text{O}$  was prepared by careful admixing of reagents in the order: sodium aluminate, 30 % NaOH solution, *n*-tetrapropylammonium bromide, demineralized water, fumed silica. A part of the freshly prepared hydrogel was centrifuged to separate the solid phase. After removal of supernatant the solid phase (gel) was washed with demineralized water and dried overnight at 100°C. The rest of hydrogel was divided into needed portions. Each of them was put into separate PTFE vessels sealed in stainless-steel reaction vessels, put into preheated oven and heated under static conditions and autogeneous pressure at 170°C for different times  $t_c$ .

Thereafter the reactors were cooled rapidly with cold water and the reaction mixture was centrifuged to separate the solid from the liquid phase. The liquid phase was carefully removed and used for measuring of silicon concentration in the liquid phase. After removal of supernatant, the solid phase was washed with cold demineralised water, dried overnight at 105°C and cooled in desiccators over dry silicagel.

Concentration of silicon in the liquid phase was measured by atomic absorption spectroscopy (AAS). X-ray diffraction patterns were recorded on a Rigaku D/Max-rB 12 kW diffractometer (Cu K $\alpha$ ). The crystallinity of the synthesized sample was calculated by the formula of (peak area between  $2\theta = 22^\circ$  and  $25^\circ$  of the product)/(peak area between  $2\theta = 22^\circ$  and  $25^\circ$  of the reference sample) $\times 100\%$ . The standard micron-sized silicalite-zeolite was used as reference. Scanning electron microscopy (SEM) measurements were performed by a Philips XL30 D6716 instrument at an operating voltage of 25 kV, while transmission electron microscopy (TEM) experiments with selected area electron diffraction (SAED) were carried out with a JEOL JEM-2010 instrument at an operating voltage of 200 kV.

## RESULTS AND DISCUSSION

Figure 1A shows that the kinetics of crystallization (change of the fraction,  $f_z$ , of crystallized zeolite ZSM-5 with the crystallization time,  $t_c$ ) is characterized by extremely long “induction period” (from  $t_c = 0$  to  $t_c = 19$  h) and by a rapid crystallization in a short time interval (from  $t_c = 19$  h to  $t_c < 21$  h). On the other hand, the change, the concentration of Si in the liquid phase of the reaction mixture during crystallization ( $C_{Si}$  vs.  $t_c$ ; see Fig. 2B) is characterized by: (i) sudden increase of  $C_{Si}$  from  $C_{Si} = 1.45$  mg/ml at  $t_c = 0$  to  $C_{Si} = 10.4$  mg/ml at  $t_c = 2$  h, (ii) slow decrease of  $C_{Si}$  from  $C_{Si} = 10.4$  mg/ml at  $t_c = 2$  h to  $C_{Si} = 9.1$  mg/ml at  $t_c = 19$  h and (iii) sudden decrease of  $C_{Si}$  from  $C_{Si} = 9.1$  mg/ml at  $t_c = 19$  h to  $C_{Si} = 6.7$  mg/ml at  $t_c = 20.667$  h. The increase of  $C_{Si}$  in the time interval from  $t_c = 0$  to  $t_c = 2$  h is caused by dissolution of amorphous silica and distribution of the various silica-containing particles between the solid and the liquid phase of the reaction mixture.

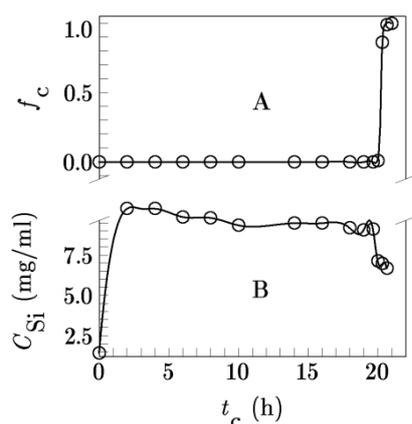


Fig.1 Change of: (A) fraction,  $f_c$ , of crystallized zeolite ZSM-5 and (B) concentration,  $C_{Si}$ , of silicon in the liquid phase.

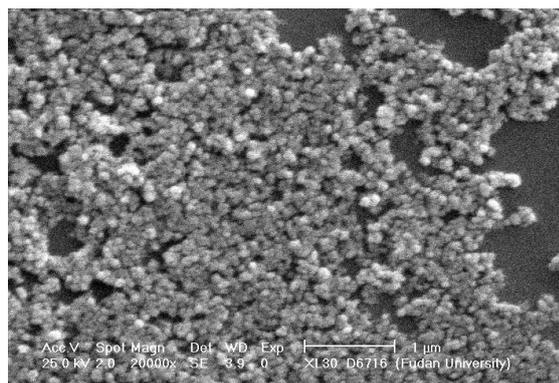


Fig. 2 SEM image of the solid phase separated from the reaction mixture at  $t_c = 2$  h.

From the composition of the reaction mixture and the concentration,  $C_{Si}$ , of silicon in the liquid phase, it can be calculated that at  $t_c = 2$  h the liquid phase of the reaction mixture contains about 45 wt. % of the silica contained in the system and the rest (about 55 wt. %) is contained in the solid phase.

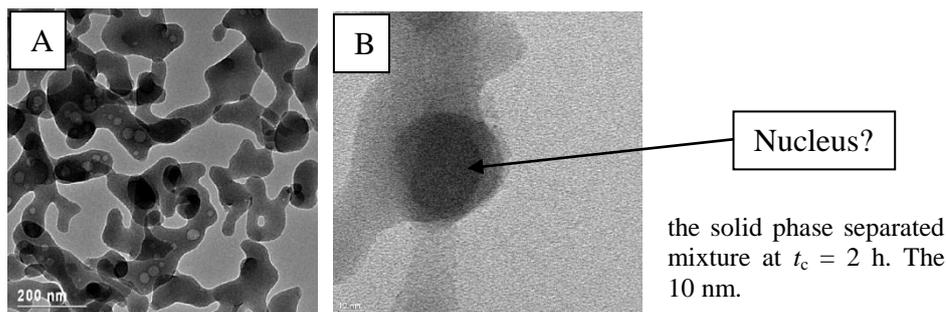


Fig. 3 TEM images of from the reaction size bar in Fig. B is

Although on the SEM image in Fig. 2 can be recognized only “discrete” particles (gathered in irregularly-shaped agglomerates) having the size in the range 40 – 150 nm, from the TEM images in Figs. 3 is evident that the solid phase is composed of 1 - 3 nm sub-colloidal particles; probably about 1 nm inorganic-organic composite species (IOCS) [5] and about 3 nm primary gel particles (composed of several IOCSs), which are precursor particles for nucleation and crystal growth of zeolite ZSM-5 [6-10]. Based on the C-model of zeolite nucleation and growth [11], we believe that precursor particles makes two “networks” in which the particles are separated by repulsive forces between themselves; outer, less dense “network” containing more charged particles and inner, denser “network” containing less charged particles. The denser “network” appears in the form of “worm-like” particles in the SEM images of the solid phase separated from the reaction mixture at  $t_c \geq 3$  h. We also believe that the spherical feature formed at the very beginning of crystallization process ( $t_c \geq 2$  h) in the denser “network” (see Fig. 3B) is nucleus of zeolite ZSM-5. Since the size of the spherical features (nuclei?) does not (considerably) change during the crystallization one can conclude that the precursor particles (P2) in the denser “network” are active for nucleation, but not for subsequent crystal growth and, in addition, that the growth of nuclei is prevented because the precursor particles (P1) active for growth are not present in the denser “network”, but are “concentrated” in the less dense one (outside of the “worm-like” particles). This is, at the same time, the reason for long “induction period” (see Fig. 1A) and constancy of the particulate characteristics of the solid phase of the reaction mixture at the SEM-observing scale; size of the worm-like particles slightly increases from  $t_c = 6$  h to  $t_c = 19$  h (see Fig. 4).

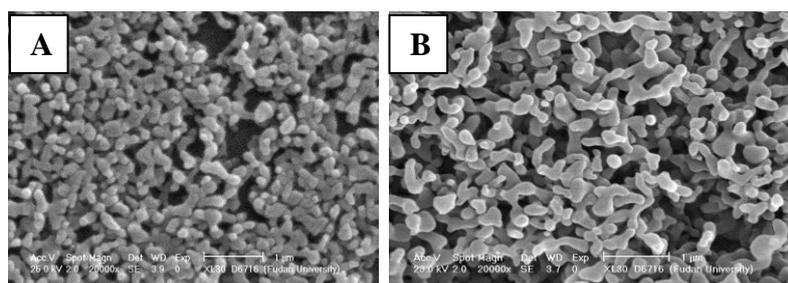


Fig.4. SEM images of the solid phase separated from the reaction mixture at  $t_c = 6$  h (A) and  $t_c = 19$  h (B)

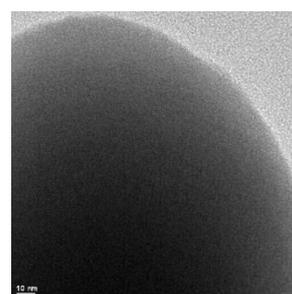


Fig. 5 TEM image of the boundary between the “worm-like” particle and less dense “network” ( $t_c = 8$  h).

On the other hand, it is really to assume that the reaction temperature (170°C) the precursor particles P1 from less dense, outer “network” slowly diffuse into denser “network” (“worm-like” particles) and the precursor particles P2 from the “worm-like” particles slowly diffuse into outer, less dense “network” (see Fig. 5). Such inter-diffusion of precursor particles between the “networks” causes a gradual equilibration in the concentration of both type of precursor particles (P1 and P2) in both “networks” and thus aggregation of the “worm-

like” particles (see Fig. 6A and 6B) and simultaneous growth of nuclei in the “worm-like” particles. These processes, which detail mechanisms are not known at the time, cause the formation of the ball-like aggregates of nano-sized ZSM-5 crystals (see Fig. 6C) as the final product of crystallization.

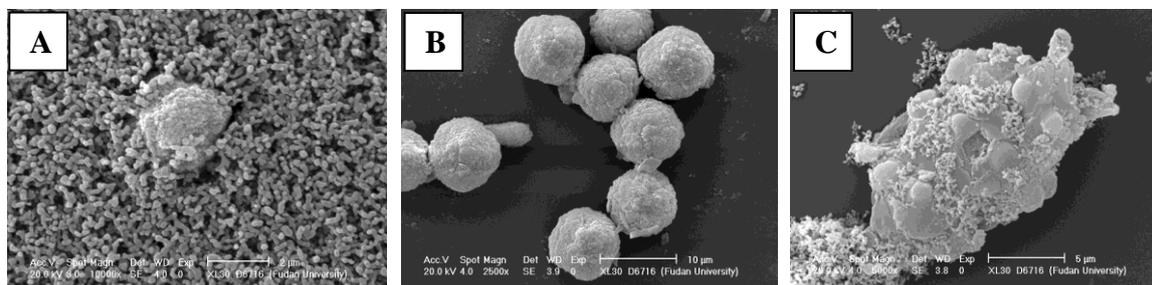


Fig. 6 SEM images of the solid phase separated from the reaction mixture at  $t_c = 19.33$  h (A),  $t_c = 20$  h (B) and  $t_c = 2.667$  h.

## CONCLUSION

Mechanism of an unusual pathway of crystallization of zeolite ZSM-5 from diluted reaction mixture was explained by assuming the formation of two “networks” of precursor particles; P1, active in crystal growth and P2, active in nucleation. Although the “networks” are separated, a slow inter-diffusion of the precursor particles occurs during the hydrothermal treatment. The equilibration of their concentrations at the end of the crystallization process causes simultaneous agglomeration of the “worm-like” particles (denser network) and rapid crystal growth of zeolite ZSM-5 and thus, formation of aggregates of nano-sized crystals of zeolite ZSM-5.

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