

## **THE ROLE OF SUB-COLLOIDAL (NANO-SIZED) PRECURSOR SPECIES IN ZEOLITES CRYSTALLIZATION**

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### **ABSTRACT**

A comparison of different approaches of the formation and evolution of sub-colloidal precursor species during crystallization of MFI-type zeolites showed that, although the formation of sub-colloidal precursor species is almost the same in both homogeneous [initially clear (alumino)silicate solutions] and heterogeneous [(alumino)silicate hydrogels], their further evolution strongly depends on the composition of the reaction mixture, especially presence (heterogeneous systems) or absence (homogeneous systems) of the solid phase as well as presence/absence of aluminium. These differences have been showed and explained through the analysis of relevant processes of crystallization of MFI-type zeolites.

Keywords: MFI-type zeolites, Sub-colloidal precursor species, Crystallization, Homogeneous systems, Heterogeneous systems

### **INTRODUCTION**

In spite of abundant amount of data obtained during 'in situ' crystallization of MFI-type zeolites in homogeneous systems,<sup>1-13</sup> and great contribution to understanding the processes occurring during the crystallization, some serious questions are still persisting. Namely, although there is a consensus about the size of primary precursor species (PPSs), i.e., about 3 nm,<sup>1-6</sup> the mechanism of their formation, their "structure", mechanism of internal structuring of individual particles and their aggregates and stage at which the nano-particles are structured, are still intensively debated objectives.<sup>1-13</sup> In addition, the results of these investigations did not answer the question how this knowledge is consistent with the crystallization of MFI-type of zeolites in heterogeneous systems. Thus, taking into consideration that knowledge on the processes which at molecular and sub-micrometer level occur in both the liquid and the solid phase of the reaction mixture during early stage of the crystallization process is extremely important for the further course of crystallization process, the objective of this contribution is investigation of the formation of nanosized precursor particles in both the liquid and the solid phases of heterogeneous reaction mixtures (hydrogels) and their evolution during crystallization of MFI-type zeolites in heterogeneous systems.

### **RESULTS AND DISCUSSION**

Results of microscopic study of the solid phase of freshly prepared reaction mixture (2.5Na<sub>2</sub>O-60SiO<sub>2</sub>-8TPABr-800H<sub>2</sub>O),<sup>13</sup> present in Fig. 1, show that the XRD and electron-diffraction amorphous solid phase represents a hierarchical structure; macro-aggregates (circumscribed by lines in Fig. 1A) having the size 400 - 1000 nm, are composed of smaller ones (circumscribed by yellow circles in Figs. 1A and 1B and/or marked by arrows in Fig. 1A) having the size of about 70 nm (Figs. 1B and 1C). The ~ 70 nm-sized aggregates are composed of about 10 nm-sized primary gel particles (Figs. 1B and 1C).

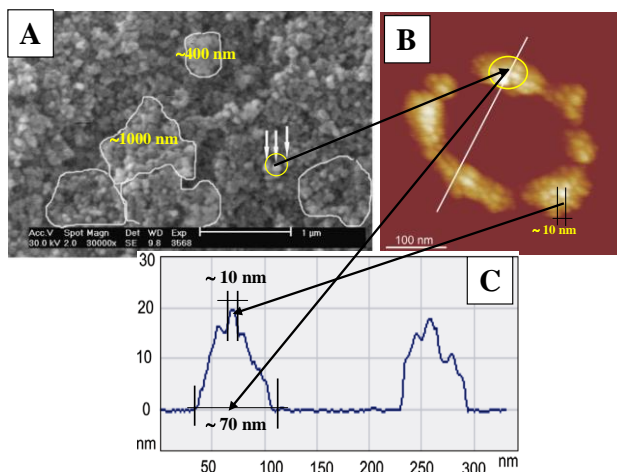


Fig. 1 SEM (A) and AFM (B) images of the solid phase of freshly prepared reaction mixture. Part C represents the section analysis of the AFM image of the part B.

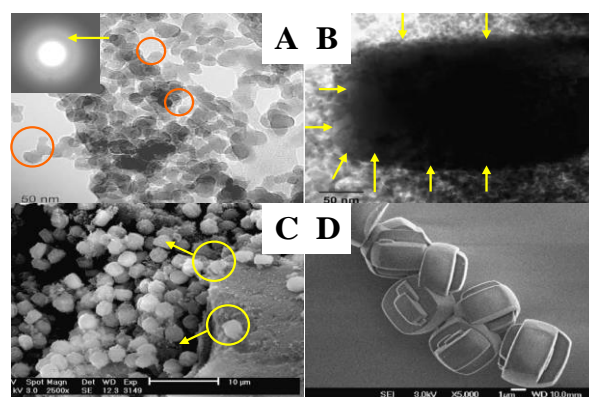


Fig. 2 TEM (A, B) and SEM (C, D) images of the solid phase of the reaction mixture, hydrothermally treated at 170 °C for  $t_c = 2$  h (A), 3 h (B and C) and 4 h (D).

Heating of the reaction mixture indicates that heating of the reaction mixture causes ordering in the part of solid phase (inset of Fig. 2A), most probably in 10 – 20 nm-sized precursor species (circumscribed by red circles in Fig. 2A) which, in this way, become viable nuclei.<sup>3,4,11</sup> Growth of the viable nuclei, by addition of surrounding growth precursor species,<sup>3,4,7,10</sup> results in the formation of the nano-sized silicalite-1 crystals inside amorphous matrix (Fig. 2B). Further growth of the silicalite-1 crystals consumes the surrounding growth precursor species (Fig. 2B) which causes de-aggregation and destroying of amorphous aggregates. The consequence is releasing of the growing silicalite-1 crystals from the amorphous matrix (Fig. 2C). The released silicalite-1 crystals continue to grow outside of the amorphous matrix (Fig. 2C) by addition of the growth precursor species formed by further de-aggregation of the remaining amorphous phase. This finally results in the formation of typical, well-shaped, micrometer-sized silicalite-1 crystals (Fig. 2D).

The solid phase of freshly prepared, Al-containing reaction mixture ( $12.5\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-60\text{SiO}_2-8\text{TPABr}-4000\text{H}_2\text{O}$ )<sup>13</sup> is composed of the un-dissolved amorphous silica (AS; Fig. 3A), used as silica source and aggregates of 3 - 20 nm-sized precursor particles (gel, circumscribed by yellow squares in Fig. 3A). The gel is, similarly as in the Al-free system, most probably formed by a chain of aggregation processes in the sequence: low-molecular (alumino)silicate anions  $\rightarrow$  ~ 3 nm-sized primary precursor species<sup>1-6,8-10</sup>  $\rightarrow$  5-10 nm-sized secondary precursor species<sup>3,4,7-10</sup>  $\rightarrow$  20 and more nm-sized particles  $\rightarrow$  gel (hierarchical assembly of amorphous precursor species of different sizes; yellow squares in Fig. 3A).<sup>3,4,7-10,11-13</sup> Heating of the reaction mixture (at 170 °C) causes: (i) further formation of precursor species of different sizes (3 – 20 nm) by both the stepwise aggregation of silicate species formed by further dissolution of amorphous silica and by de-aggregation of the amorphous aggregates (gel) formed at room temperature and (ii) formation of worm-like particles (WLPs; Figs. 3B and 3C) by "directed" aggregation of the precursor species.<sup>13</sup> At the early stages of heating, e.g.,  $t_c < 4$  h, the un-dissolved amorphous silica, remaining gel and formed WLPs exist in some kind of "network" (Figs. 3B and 3C). Since the "connective elements" of the nanosized particles in the "network" is undissolved silica, its further dissolution causes the "destroying" of "network" so that the WLPs exist as discrete entities, having the size about 200 nm, at  $t_c \geq 4$  h (Fig. 4A).

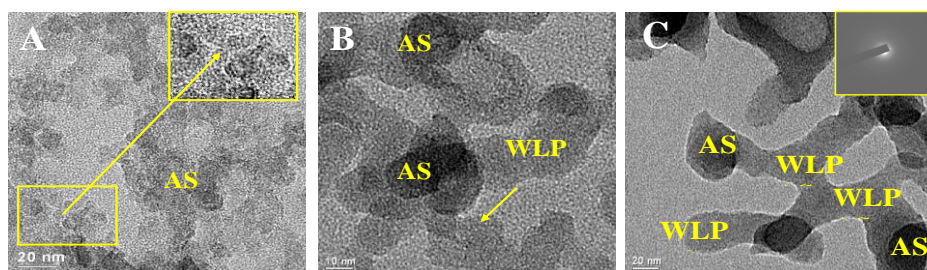


Fig. 3 TEM images of the solid phase of freshly prepared reaction mixture (A) and of the same reaction mixture hydrothermally treated at 170 °C for  $t_c = 1$  h (B) and 2 h (C). AS = amorphous silica, WLP = worm-like particles

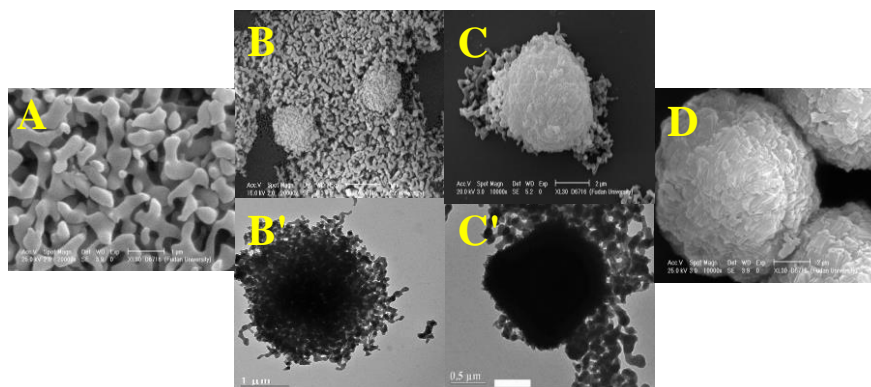


Fig. 4 SEM (A,B,C,D) and TEM (B'C') images of the solid phases of reaction mixture hydrothermally treated at 170 °C for  $t_c = 18$  h (A),  $t_c = 20.33$  h (B,B'),  $t_c = 20.66$  h (C,C'), and  $t_c = 21$  h (D).

Prolonged heating induces aggregation of WLPs and formation of their rickety aggregates (Figs. 4B and 4B') at  $t_c = 20.33$  h and subsequent formation of condensed aggregates (CAs; Figs. 4C and 4C') caused by coalescences of WLPs in rickety aggregates. High concentration of aluminosilicate material in CAs is favourable for the formation of nuclei and their growth inside amorphous matrix of CAs. Simultaneous growth of a large number of nuclei in each of the CAs results in the formation of polycrystalline aggregates of zeolite ZSM-5 (Fig. 4D).

## CONCLUSION

Although, the formation of sub-colloidal precursor species in heterogeneous systems (hydrogels) is, generally, the same or similar as in homogeneous systems (initially clear (alumino)silicate solutions), their evolution during hydrothermal treatment strongly depends not only on the presence of the solid phase, but is also extremely sensitive on the presence of aluminum in the reaction mixture. In the absence of Al (crystallization of silicalite-1), a small fraction of 10-20 nm-sized precursor species transforms, by internal restructuring, into viable nuclei which then grow by addition of the remaining growth precursor species. This results in crystallization of discrete, micrometer sized crystals of silicalite-1. Although in the presence of Al the formation of primary amorphous precursor (gel) is almost the same as in absence of Al, further evolution of the solid phase during heating is quite different and takes place in the sequence; (i) deaggregation of primary amorphous precursor (gel), (ii) formation of secondary amorphous precursor (worm-like particles – WLPs), (iii) formation of tertiary amorphous precursor (condensed aggregates - CAs) by aggregation of the WLPs and densification

(condensation) of aggregates, and (iv) formation of nuclei and their growth in the matrixes of CAs; these processes result in the formation of fully crystalline zeolite ZSM-5 in the form of polycrystalline aggregates. Hence, it is evident that presence of aluminium in the reaction mixture completely changes the pathway of crystallization of MFI-type zeolites. From this reason, further investigation will be focused to the role of Al in the evolution of subcolloidal precursor species during the synthesis of MFI and other types of zeolites.

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