A CONTRIBUTION TO UNDERSTANDING THE MECHANISM OF ZEOLITES CRYSTALLIZATION

Boris Subotić[1], Sanja Bosnar[1], Josip Bronić[1], Tatjana Antonić Jelić[1], Nan Ren[2]

[1]Ruđer Bošković Institute, Division of Materials Chemistry, Laboratory for the Synthesis of New Materials, Bijenička 54, 10000, Zagreb, Croatia

[2]Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Institute of Catalysis and Laboratory of Advanced Materials, Fudan University, Shanghai, 200433, P. R. China

E-mail: subotic@irb.hr

ABSTRACT

Structural, morphological and particulate properties of the intermediates formed during the crystallization of zeolite ZSM-5 under different conditions, but also during crystallization of some other types of zeolites, showed that in all the investigated systems the crystallization takes place by the reaction sequence: "gel" $\Rightarrow$ worm-like particles (WLPs) $\Rightarrow$ condensed aggregates (CAs) $\Rightarrow$ crystalline end product(s). The differences between the crystallization pathways and the properties of intermediates ("gel", WLPs, CAs) and products can be readily explained by the analysis of the known and/or assumed influences of the components of the reaction mixture on each of the relevant sub-process.

Keywords: Zeolite, Crystallization, Mechanism, Worm-like particles, Condensed aggregates

INTRODUCTION

Recent investigation of the mechanism of crystallization of zeolite ZSM-5 in a dilute heterogeneous reaction mixture (RM0 having the chemical composition: $12.5Na_2O:Al_2O_3:60SiO_2:8TPABr:4000H_2O$) has shown that the crystallization process takes place by a chain of processes: (i) formation of "gel" (primary amorphous precursor) at room temperature, (ii) formation of "worm-like" particles (WLPs, secondary amorphous precursor) at increased temperature (170 °C), (iii) formation of condensed aggregates (CAs, tertiary amorphous precursor) by aggregation/coalescence of WLPs 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 of very small, nano-sized crystals of zeolite ZSM-5 [1]. Later on, it was shown that the formation of WLPs is a very complex event which takes place by a series of dissolution-aggregation processes [2]. Since some "elements" (WLPs, spherical amorphous particles, polycrystalline aggregates) of the described reaction sequence [1] also appear in the appropriate literature [3-10], we assumed that the reaction sequence (i) - (iv) is characteristic not only for crystallization of zeolite ZSM-5 in dilute heterogeneous systems, but that is imminent for the majority of the crystallization systems of the general composition: $aR_2O:bAl_2O_3:cSiO_2:dSDA:eH_2O$, where R is inorganic and/or organic cation and SDA is structure-directing agent. To prove (or disapprove) the above assumption, we analyzed the structural, morphological and particulate properties of the intermediates during crystallization of zeolite ZSM-5 under different conditions, but also during the crystallization of some other types of zeolites different from zeolite ZSM-5. The differences between the crystallization pathways and the properties of intermediates are discussed with respect to the chemical compositions of the reaction mixtures and crystallization conditions.

EXPERIMENTAL

Reaction mixtures (hydrogels; $aR_2O:bAl_2O_3:cSiO_2:dSDA:eH_2O$) were prepared by mixing together appropriate amounts of freshly prepared solution of sodium or potassium hydroxide (30 wt. %), sodium aluminate, SDA (tetrapropylammonium bromide - TPABr, 1,8-diaminooctane – 1,8-DAO or ethylenediamine - EDA) and fumed silica ($300 - 400$ m^2/g), under vigorous stirring at room temperature. Such prepared reaction mixtures (RMs) were additionally stirred at room temperature for 1 h and then, were divided among needed number of autoclaves, then were put into an oven preheated at crystallization temperature (160 - 177 °C) and hydrothermally treated under static and/or dynamic conditions. At predetermined crystallization times, t_c, the selected autoclaves were taken out from the oven and cooled down to the ambient temperature. After cooling the autoclave, the solid phase was separated from the liquid phase by centrifuging. After washing and drying (at 80 °C for 10 h), the solid phases were characterized with respect to their structural, morphological and particulate properties. The X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max-rB 12 kW diffractometer (Cu Kα). Scanning electron microscopy (SEM) analyzes were performed by a Philips XL30 D6716 instrument at an operating voltage of 25 kV. Field-emission scanning electron microscopy (FE-SEM) analyzes were performed by FEI Nova NanoSEM instrument. Particle size distribution (PSD) curves were determined with a Malvern Mastersizer 2000 laser light-scattering (LLS) particle size analyzer.

RESULTS AND DISCUSSION

Previously has been shown that the solid phase ("gel") formed during short-time (1 h) room-temperature ageing of RM0 transforms into about 200 nm-sized WLPs during four hours of hydrothermal treatment of the RM0 at 170 °C; the WLPs can be clearly observed in the SEM image made at the magnification of 20000× [1,2]. A reduction of water content form $[SiO_2/H_2O]_b = 60/4000 = 0.015$ in RM0 to $[SiO_2/H_2O]_b = 60/800 = 0.075$ in the RM: $2.5Na_2O:Al_2O_3:60SiO_2:8TPABr:800H_2O$ (RM1), at the constant batch molar alkalinity (A = $[Na_2O/H_2O]_b = 0.003125$) shortens the overall crystallization time for about 2.5 times (Fig. 1) and, at the same time, drastically decreases the size of WLPs so that they cannot be clearly observed in the SEM image made at the magnification of 20000× (Fig. 1B), but only in the FE-SEM image made at the magnification of 120000× (Fig. 1C). In fact, SEM images of "gel" (Fig. 1A) and WLPs (Fig. 1B) look almost the same when they are made at the magnification of 20000×. This is, at the same time, a possible explanation why the WLPs have not been observed and thus, recognized as the specific particle population in many previous studies [5-8]. The WLPs, formed during 2 h of hydrothermal treatment of RM1 at 170 °C transform into near-spherical, amorphous CAs at $t_c = 4$ h (Fig. 1D) and further ($t_c = 8$ h), into fully crystalline zeolite ZSM-5 appearing in the form of polycrystalline aggregates (Fig. 1E) composed of small, sub-micrometer-sized crystals of zeolite ZSM-5 (Fig. 1F). Reduction of the content of tetrapropylammonium bromide TPABr) and increase of the batch molar alkalinity do not change the general sequence characteristic for RM0 [1] and RM1 (see Fig. 1), i.e., "gel" ⇨ WLPs ⇨ CAs ⇨ crystalline end product(s).
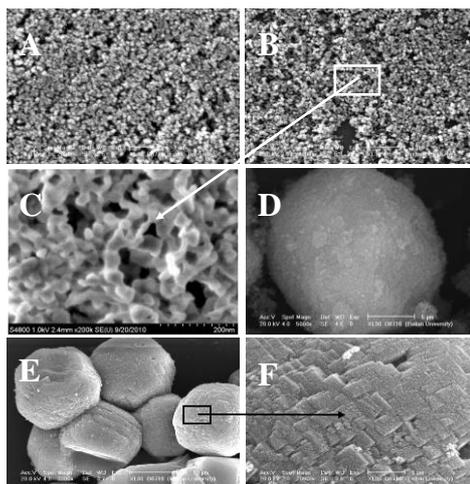
Figure 1. Scanning-electron microscopy (SEM) image of the solid phase of the reaction mixture (RM): $2.5Na_2O:Al_2O_3:60SiO_2:8TPABr:800H_2O$ aged at room temperature for 1 h (A) and of the same RM hydrothermally treated at 170 °C for 2 h (B, C), 4 h (D) and 8 h (E, F). Magnifications: 3000× (E), 5000× (D), 20000× (A, B, F) and 12000× (C).
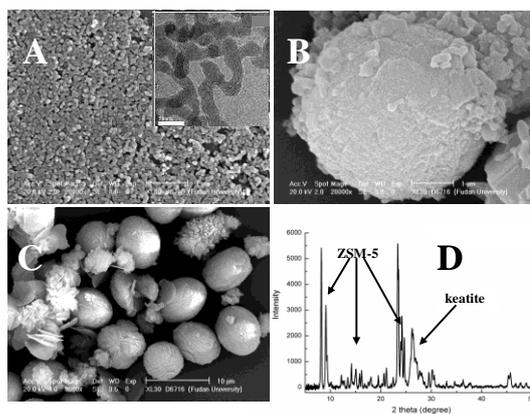
Figure 2. Scanning-electron microscopy (SEM) images of the solid phases of the reaction mixture (RM): $12.5Na_2O:Al_2O_3:60SiO_2:4000H_2O$ hydrothermally treated at 170 °C for 2 h (A), 70 h (B) and 92 h (C). The inset of Fig. 2A represents the corresponding TEM image. Magnifications: 20000× (A, B) and 3000× (C). Fig. D represents the XRD pattern of the solid phase (product) shown in Fig. C.

However, the overall crystallization time increases with the reduction of the content of TPABr. In addition, although the WLPs (Fig. 2A) and CAs (Fig. 2B) form in the absence of TPABr, the product of crystallization is not pure zeolite ZSM-5, but a mixture of the polycrystalline aggregates of zeolite ZSM-5 and typical plate-like particles of keatite [11] (Figs. 2C and 2D). An increase of the batch molar alkalinity of RM0 from $A = 0.003125$ to 0.006 and 0.009 causes the crystallization of an aluminosilicate crystalline phase which structural and morphological properties considerably differ from the corresponding properties of zeolite ZSM-5. Finally, drastic change of the chemical composition of the RM (e.g., replacement of Na^+ ions with K^+ and use of electrically neutral template molecules (1,8-DAO or EDA) instead of TPABr, increase/decrease of crystallization temperature and the change of "mechanical" conditions (crystallization under static or dynamic conditions) do not change the general reaction pathway;

"gel" ⇨ WLPs ⇨ CAs ⇨ crystalline product. However, the rates of particular sub-processes (formation of WLPs, their transformation to CAs and transformation of CAs to the crystalline end product), the overall crystallization time and the structural and morphological properties of the obtained products considerably depend on the above mentioned factors. On the basis of the analysis of the changes of structural, morphological and particulate properties of the intermediates as well as the crystalline end products obtained during hydrothermal treatment of 13 different reaction mixtures under different conditions, it was concluded that in all investigated systems, the crystallization takes place by the chain of processes: "gel" ⇨ WLPs ⇨ CAs ⇨ crystalline end product(s). Although this crystallization pathway seems, at the first sight, more complex than the existing one (formation and growth in the primary amorphous precursor (gel) and/or the "secondary amorphous phase" formed by equilibration of the primary amorphous phase with the liquid phase during room-temperature ageing and/or initial heating of RM [11,12]) it enables rational explanation of the observed events/changes by specific influences of the components of the reaction mixtures on the particular sub processes (formation of "gel", transformation of gel to WLPs, transformation of WLPs to CAs and formation of crystalline end product by its nucleation crystal growth in the matric of CA).

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