

CONTRIBUTION TO UNDERSTANDING THE MECHANISM OF SDA-FREE, SEED-INDUCED SYNTHESIS OF SUB-MICROMETER SIZED ZSM-5 ZEOLITES

Nan Ren^{1,2}, Boris Subotić², Josip Bronić²

¹Fudan University, 220 Han Dan Road, 200433 Shanghai, P. R. China

²Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia

E-mail: nanren@fudan.edu.cn (N.Ren) and subotic@irb.hr (B. Subotić)

ABSTRACT

The seed-induced crystallization system has been adopted for the synthesis of sub-micrometer sized zeolite ZSM-5 in the absence of organic structure directing agent (SDA). The structural (phase purity), particulate (sizes and morphologies) and chemical compositions (framework Si/Al ratios) of the crystalline end products could be well controlled via the variation of synthesis parameters such as size and amount of silicalite-1 seed nanocrystals, batch alkalinity, excess of sodium ions and ageing of reaction mixtures. More importantly, the crystallization mechanism has also been revealed as a typical linear, size-independent growth process on the surface of silicalite-1 seed nanocrystals, embedded in the gel matrix, without the formation of new nuclei either on the surface of growing seed crystals or in the gel matrix. The critical processes happened during crystallization have also been characterized by different methods and evaluated by population balance modeling approach.

Keywords: zeolite ZSM-5; crystallization; modeling; controllable synthesis; mechanism.

INTRODUCTION

As an important member in the family of crystalline tectoaluminosilicate framework, zeolite ZSM-5 exhibits special 'shape-selectivity' in many key catalytic processes such as alkylation, dewaxing, toluene disproportionation etc [1]. In recent years, investigations of correlation between crystal size and reactivity of ZSM-5 zeolites showed that, catalytic activity increases with decreasing of crystal size while the selectivity exhibits a reverse trend. Thus, an ideal ZSM-5 based zeolitic catalyst should be a compromise between the activity and selectivity or, in other words, sub-micrometer sized zeolite ZSM-5 seems to be a quite interesting candidate for the realization of high catalytic efficiency [2]. To precise control the properties of the crystalline end products, mechanism of crystallization, especially the critical processes occurring during the crystallization must be clearly understood. On the other hand, in order to reduce the production cost and to avoid the pollution during removal of SDA through calcinations, thus, an ideal approach for the synthesis of sub-micrometer sized zeolite ZSM-5 should be performed in the SDA-free batch. From the above reasons, recently, we proposed a seed-induced approach for the synthesis of zeolite ZSM-5 in the SDA-free synthesis system [3-5]. Since such approach is a promising applicable candidate for the synthesis of high performance ZSM-5 based zeolitic catalyst, here, the state-of-art contributions have been introduced in detail for the understanding of the "mysteries" of the synthesis system.

EXPERIMENTAL

The synthesis was carried by preparation of a reaction mixture (hydrogel) with the composition of $1.0\text{Al}_2\text{O}_3/100\text{SiO}_2/x\text{Na}_2\text{O}/4000\text{H}_2\text{O}$ in which the batch alkalinity, expressed as $A = [\text{Na}_2\text{O}/\text{H}_2\text{O}]_b$ was adjusted through varying the value of x . After the hydrogel was prepared, different amounts (4, 8, 16 and 32 wt.% relative to total amount of silica in the reaction mixture) of silicalite-1 seed crystals having different sizes were added. The prepared reaction mixtures were additionally stirred at room temperature for different times (t_a), then

were transferred to autoclaves and heated under auto-generous pressure at 483 K for 2 h. After cooling the autoclave, the product was separated by filtration and washed. The as-synthesized samples were dried at 353 K for 1 day, and characterized by SEM (Scanning Electron Microscopy), TEM (Transmission Electron Microscopy), XRD and PSD. Parts of the fresh gel prepared at different alkalinities were also washed, collected and characterized for comparison.

RESULTS AND DISCUSSION

Figure 1 shows the SEM images of used silicalite-1 seed crystals having different sizes (left) and of a typical product obtained from the reaction mixture: $1.0\text{Al}_2\text{O}_3/100\text{SiO}_2/28\text{Na}_2\text{O}/4000\text{H}_2\text{O}$ ($x = 28$), using 4 wt. % of silicalite-1 seed crystals with average diameter of about 260 nm (right). It can be clearly observed that, the sizes of the seeds are well adjusted and that the fully crystalline end product is obtained in no more than 2h of hydrothermal treatment at 483K. Such high reaction rate also renders the approach with industrial efficiency.

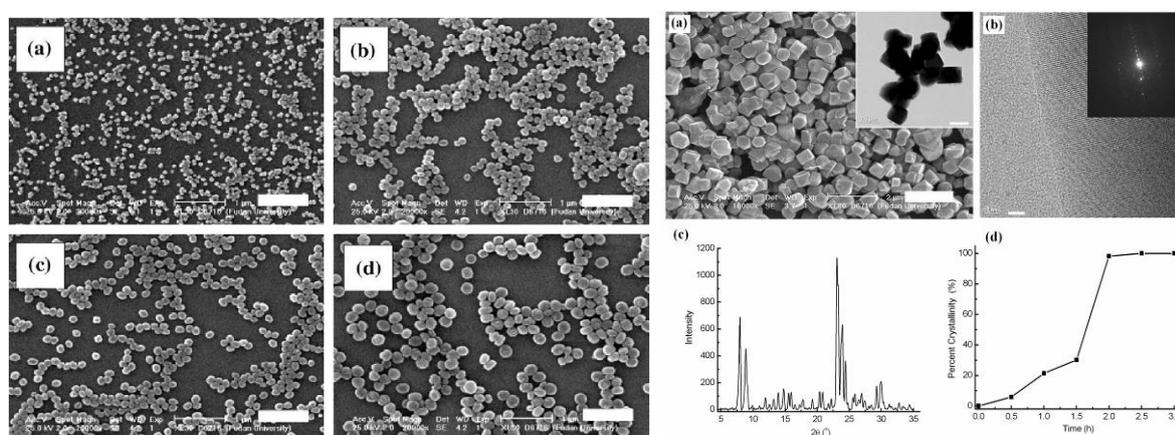


Figure 1. Left: silicalite-1 seed (nano)crystals with diameter of 90 (a), 180 (b), 220 (c), and 260 nm (d), synthesized by clear-solution method. Right: SEM (a) and, TEM (inset of a and b) images, and XRD pattern (c) of the product obtained by using 4 wt. % of silicalite-1 seed crystals (260 nm). Relevant crystallization curve is shown in (d).

Table 1. Correlation between size/amount of silicalite-1 seed crystals and properties (size, shape) of the crystalline end products.

Seed size (nm)	Amount of seeds (wt.% of silica in the batch)	Size of crystalline end products (nm) ^a	Particulate property ^a
90	4	270	Round shape
180	4	350	Hexagonal box
220	4	440	Hexagonal box
260	4	520	Hexagonal box
260	8	440	Hexagonal box
260	16	410	Round shape
260	32	350	Round shape
690	4	1100	Hexagonal box

Note: Batch gel composition is: $1.0\text{Al}_2\text{O}_3/100\text{SiO}_2/28\text{Na}_2\text{O}/4000\text{H}_2\text{O}$. ^aObserved and calculated from corresponding SEM images.

Since the properties of products strongly depend on the size and amount, respectively of seed crystals [6], these parameters were varied to obtain the crystalline end products with different size and morphology. Table 1 shows a correlation between size/amount of seeds crystals and properties of the crystalline end products. The results clearly indicate that the size of the final product increases with increasing of seed size, while decreases with increasing amount of seed crystals. Also, the particle shape of the products is strongly related to the investigated parameters. These phenomena are in agreement with the well-documented effects of seeding in the synthesis of zeolites [6].

Although, taking into consideration well established correlation between the size/amount of seed crystals and particulate properties of products, the later ones can be relatively well controlled, however, for a rational prediction and control of the product properties, the critical processes which occur during crystallization must be understood as well. This understanding can be realized by: (i) study of the evolution of intermediates during crystallization process; and (ii) study of the influence of hydrogel composition parameters on the product properties.

The evolution of intermediates was investigated by TEM (Figure 2 – left) and XRD (Fig. 2 – right) characterizations of the solid samples separated from the reaction mixture (4 wt. % of 260 nm seed crystals; $x = 28$) at various crystallization times, t_c . Microscopic (TEM) analysis shows that two nanometer sized particle populations, namely larger seed crystals and smaller particles of amorphous precursors can be identified at initial stage of crystallization (Figure 2a – left). During heating of reaction mixture, amorphous precursor particles agglomerate around the seed crystals and, at the same time, deposit onto the surfaces of seed crystals, thus forming growing ‘core-shell’ intermediates (Figures 2b and 2c – left). Although embedded in the gel matrix, the edges of product crystals can be clearly distinguished from the amorphous phase at later stages of crystallization process (Figures 2c and 2d).

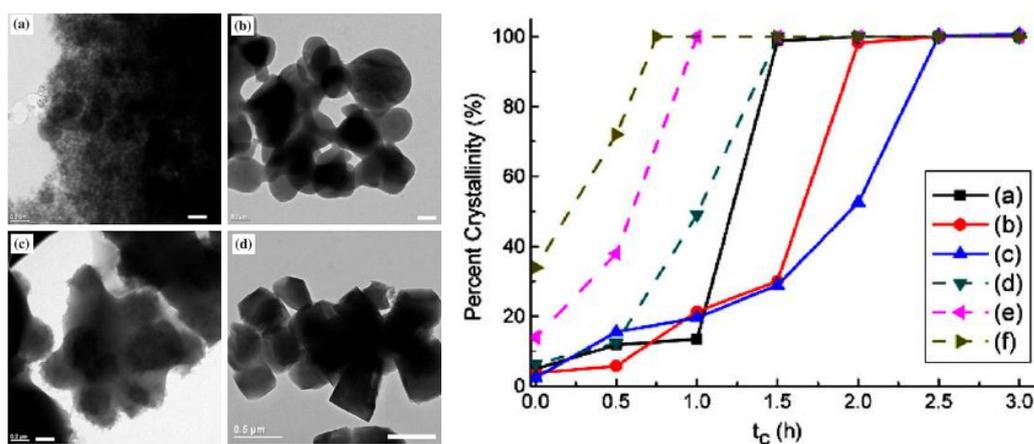


Figure 2. Left: TEM images of the solid phases separated from the reaction mixture (4 wt. % of 260 nm seed crystals; $x = 28$) at $t_c = 0.5$ h (a), $t_c = 1.0$ h (b), $t_c = 1.5$ h (c), and $t_c = 2.0$ h (d) of crystallization duration; Right: Influence of size/amount of silicalite-1 seed crystals on the rate of crystallization at (a) 4 wt.% 90 nm seeds, (b) 4 wt.% 260 nm seeds, (c) 4 wt.% 690 nm seeds, (d) 8 wt.% 260 nm seeds, (e) 16 wt.% 260 nm seeds, and (f) 32 wt.% 260 nm seeds.

On the other hand, the corresponding crystallization curves (Fig. 2 – right) clearly show that, the rate of crystallization increases either with decreasing seed size and/or with increasing seed amount. Taking into consideration the suppression of nucleation tendency in the presence of seeds, the crystallization of zeolite ZSM-5 from TPA-free reaction mixture in the presence of silicalite seed crystals is a seed-surface growth process which takes place by linear, size-independent growth of the seed crystals embedded in the gel matrix, as also

revealed by very well, or almost excellent agreement between calculated (simulated) kinetics of crystallization (f_c vs. t_c functions) and particulate properties (particle size distribution) of the crystalline end products and the measured kinetics and particulate properties.

In the study of the influence of hydrogel composition on the product properties, attention is paid to variation of product properties with the batch alkalinity, A . At low alkalinities ($A \leq 0.005$), only the mixtures of amorphous phase (major) and MFI phases (minor) could be obtained ($A \leq 0.005$), while phillipsite co-crystallizes with MFI at high alkalinities ($A \geq 0.011$). In the alkalinity range of $0.006 \leq A \leq 0.01$, crystallizes pure zeolite ZSM-5 having different Si/Al ratio; the Si/Al decreases from 18 to 10 when alkalinity increases from $A = 0.006$ to $A = 0.01$.

Analysis of either the experimentally obtained and simulated (calculated) data has shown that the seed-induced, SDA-free crystallization of zeolite ZSM-5 can be described as a five-step process: (i) dissolution of the amorphous precursor, (ii) formation of (alumino)silicate gel by polycondensation reactions, (iii) formation of 5-1 secondary building units, and their condensation into active growth precursor species in the gel matrix, (iv) deposition of the growth precursor particles from the amorphous shell onto the surfaces of silicalite-1 seed crystals and (v) "ordering" of the deposited growth precursor particles by the gradual transformation from amorphous phase to fully crystalline phase (zeolite ZSM-5).

CONCLUSION

Seed-induced, SDA-free crystallization of sub-micrometer sized zeolite ZSM-5 can be revealed as a seed surface crystallization which takes place by a size-independent growth of seed crystals embedded in the gel matrix (core-shell growth mechanism) without the occurrence of nucleation process. The growth precursor species are probably 5 – 10 nm secondary particles formed by condensation of 5-1 secondary building units. The product properties (size, shape and Si/Al ratio) can be successfully controlled by variation of the synthesis parameters such as size and amount of seed crystals and batch alkalinity. Such, a well discovered and understood, high efficient synthesis approach endows the material with promising industrial applicability.

REFERENCES

- [1] N.Y. Chen, W.E. Garwood and F.G. Dwyer, *Shape Selective Catalysis in Industrial Applications*, 2nd edition, Marcel Dekker Inc., New York, 1996.
- [2] F. D. Renzo, *Catal. Today* 1998, **41**, 37-40.
- [3] N. Ren, Z.-J. Yang, X.-C. Lv, J. Shi and Y.-H. Zhang and Y. Tang, *Micropor. Mesopor. Mater.*, 2010, **131**, 103-114.
- [4] N. Ren, J. Bronić, B. Subotić, X.-C. Lv, Z.-J. Yang Y. Tang, *Micropor. Mesopor. Mater.*, 2011, **139**, 197-206.
- [5] N. Ren, J. Bronić, B. Subotić, Y.-M. Song, X.-C. Lv and Y. Tang, *Micropor. Mesopor. Mater.*, 2011, in press.
- [6] S. Gonthier and R. W. Thompson, *Stud. Surf. Sci. Catal.*, 1994, **85**, 43-50.