Rapid synthesis of small crystal FeZSM-5 by a two-stage varying-temperature technique

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Small crystal FeZSM-5 was synthesized by a two-stage varying-temperature technique, in which the reaction mixture was first kept at a relatively low temperature for a period, and then abruptly raised to the required crystallization temperatures. The effects of sol concentration, alkalinity, temperature as well as templates on crystal size were investigated. The results showed that the crystal size of the ultimate product could be tailored through controlling the nucleation period and rate in the first stage via changing alkalinity, templates, and water content in hydrogel. Typically, a product with uniform crystal size of about 300 nm was obtained from a reaction mixture with molar ratio $1SiO_2 : 0.02Fe_2O_3 : 0.6R : 0.3Na_2O : 50H_2O$ ($R = n$-butylamine) under suitable crystallization conditions for 50 h.

Keywords: FeZSM-5 synthesis, FeZSM-5 small crystals

1. Introduction

Zeolites and related microporous materials have been extensively used as catalysts. Recently, much effort has been devoted to the synthesis, characterization and application of metallosilicates containing elements in the framework other than Al (Si), such as Fe, Ga, B, Ti, V, etc. [1–5]. The new materials thus produced have different catalytic behavior with altered activity, selectivity and stability. Among the metallosilicates, FeZSM-5 has been extensively studied as reviewed by Ratnasamy et al. [6], and showed potential applications as catalysts in oligomerization of C_2–C_4 olefins [7], MTO [8] and dewaxing [9] processes.

The crystal size of zeolites has significant influence on their properties. In practice, a small crystal zeolite catalyst may be preferred to enhance its activity and stability. Ratnasamy et al. [10] reported a decrease in ZSM-5 activity in xylene isomerization with increasing crystal size and attributed the activity decay to diffusion control. The same trend has been reported by Herrmann [11] in the MTO, n-hexane isomerization and methanol amination reactions. Generally, small crystal has some advantages over larger crystal as summarized by Renzo [12]: (a) catalyst effectiveness is larger; (b) diffusion of matrix components is easier; (c) template extraction, cation exchange are more easily performed; (d) deactivation caused by coke deposition is not so severe; and (e) regeneration of used catalysts can be easier for smaller crystals.

Although significant advances have been made in understanding the catalytic properties of zeolites and related microporous materials, little is known about the complex phenomena involved in their crystallization process, especially for zeolites containing Fe, Ga, B, etc., in the frameworks. The conventional hydrothermal method of zeolite synthesis usually yields micrometer-sized crystals. Li et al. [13] reported the synthesis of nanometer-sized silicalite-1 with short synthesis time and high yields by a two-stage varying-temperature crystallization procedure.

In our previous paper [14], Fe-silicalite-1 was synthesized by using a two-stage varying-temperature method, in which the reaction mixture was first kept at a relatively low temperature for a period, and then abruptly raised to the required crystallization temperatures. The incorporation of iron atoms in the lattice sites was confirmed by FTIR, Mössbauer spectra and XRD techniques. In the present paper, the rapid synthesis of small crystallite FeZSM-5 zeolite by the same preparation method is reported in detail. The effects of sol concentration, alkalinity, temperature as well as templates on crystal size are investigated.

2. Experimental

2.1. Synthesis

The synthesis was carried out by a two-stage varying-temperature technique described as follows. The silicon source was sodium silicate and the iron source a solution of ferric nitrate. The reaction hydrogel was prepared by adding the sodium silicate solution dropwise into the acidic solution ($pH < 2$, adjusted by sulfuric acid) of ferric nitrate with stirring to form the ferrisilicate complex. After 30 min of vigorous stirring, the pH value of the reaction mixture was increased to the required value for synthesis by adding diluted NaOH solution. After another 30 min of stirring, certain amount of aqueous solution of n-butylamine, ethylenediamine or hexanediamine, serving as organic structure-directing agent, was added. The mixture was stirred again for 2 h and then transferred into a 5 l stainless autoclave with stirring. A sampling valve was amounted to the autoclave which enables one to sample during synthesis without interrupting the reaction system. The autoclave was first raised to 120 °C at a heating rate of 20 °C/h and held for a certain period. Then it was abruptly raised to 160–180 °C and held for more than 40 h. At last, the autoclave was quenched by water and the solid product was centrifugally separated, washed and dried overnight at 120 °C.

The conventional one-stage synthesis was also carried out for comparison, in which the reaction mixture was raised directly to the synthesis temperature at a heating rate of 20 °C/h. The agitation rate of the autoclave was 500 RPM throughout the experiments.

2.2. Characterization

The product was identified by X-ray powder diffraction using a D/max-γA diffractometer with Cu Kα radiation in the range of 2θ between 5° and 40°. The crystallinity was calculated according to the method described in [15].

Scanning electron micrographs were obtained on a Hitachi H-600-2 scanning microscope. Crystal size and distribution measurements in the range of 3–3000 nm were carried out by means of laser light diffraction with a Coulter N4 plus size analyzer. A suspension of zeolite in distilled water was prepared and subject to ultrasonic vibration before crystal size distribution evaluation.

The ^{57}Fe Mössbauer measurements were performed using a conventional constant acceleration spectrometer with ^{57}Co in Rh. Spectra were recorded in zero field at room temperature relative to pure metallic iron. Fits were performed using a standard least squares fitting routine. Average isomer shifts were calculated from the fits.

3. Results and discussion

Mössbauer spectroscopy of the ^{57}Fe atom is ideally suited for the study of ferrisilicates. The isomer shift parameter (IS), resulted from the electrostatic interaction between the charge distribution of the nucleus and those electrons which have a finite probability of being found in the region of the nucleus, is sensitive to the extranuclear environment. It thus provides a useful method for determining the valency and oxidation state of the Fe atom. Meagher et al. [16] proposed a simplified criterion for determining whether the iron was incorporated into the zeolite framework, i.e., (1) Is the sample white in color? and (2) Is the average IS (RT) $\approx$ 0.25 mm/s? All of our samples with a Si/Fe ratio of 25 were white in color. The Mössbauer spectra recorded at room temperature showed either a singlet or a doublet for these samples obtained from both one-stage and two-stage synthesis methods. The IS values ranged from 0.23 to 0.26. These data thus indicated that almost all the iron was in tetrahedrally coordinated lattice sites according to the proceeding criterion. A spectrum of a sample prepared according to the procedure described in section 3.6 is shown in figure 1. The IS for this sample was 0.23 mm/s relative to pure Fe and the half peak width (FWHM) was 1.06 mm/s. The main efforts of this study will be focused on the investigation of the influence of synthesis conditions on crystallite size.

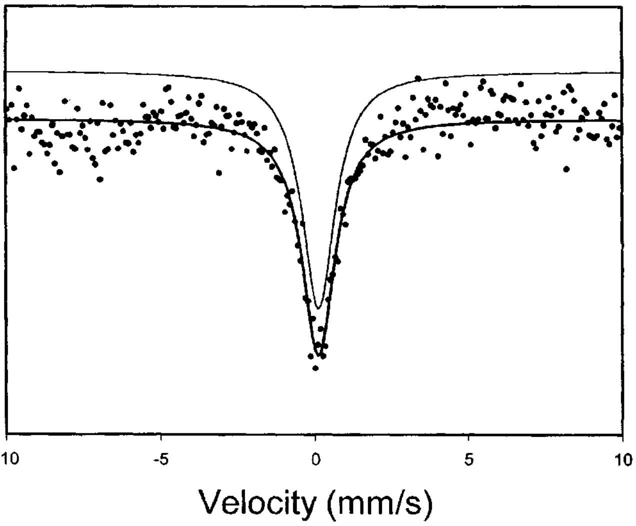

Figure 1. Mössbauer spectrum of FeZSM-5 (Si/Fe ratio of 25) recorded at room temperature.

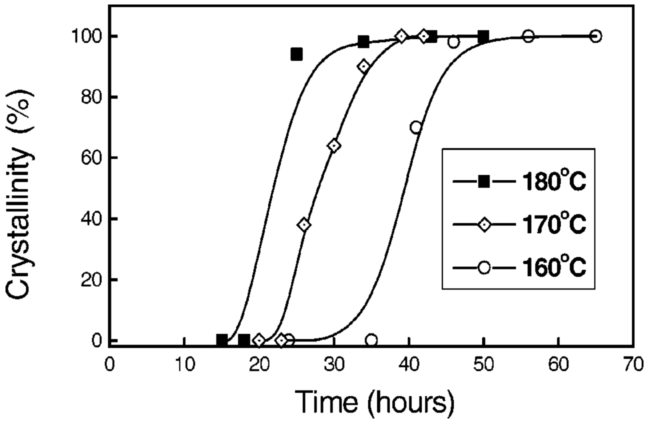

Figure 2. Crystallization curves of FeZSM-5 by conventional one-stage method at various temperatures.

3.1. Effect of temperature on one-stage synthesis

Figure 2 shows the time dependence of crystallinity of FeZSM-5 obtained by the conventional one-stage method at various temperatures. The chemical composition of the reaction mixture was $1SiO_2 : 0.02Fe_2O_3 : 0.6R : 0.3Na_2O : 50H_2O$ (R = n-butylamine). Obviously, an induction period existed for each run and was in dependence of temperature as expected. Upon raising the temperature, the induction period was shortened, and the average crystal size increased with temperature, as shown in figure 3. From the

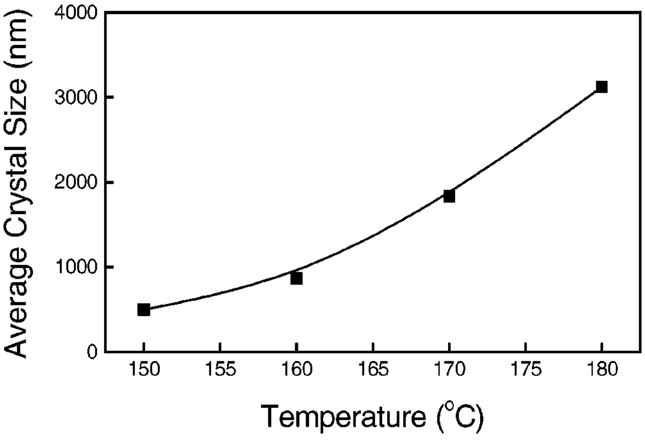

Figure 3. Plot of average size versus temperature of the one-stage synthesis.

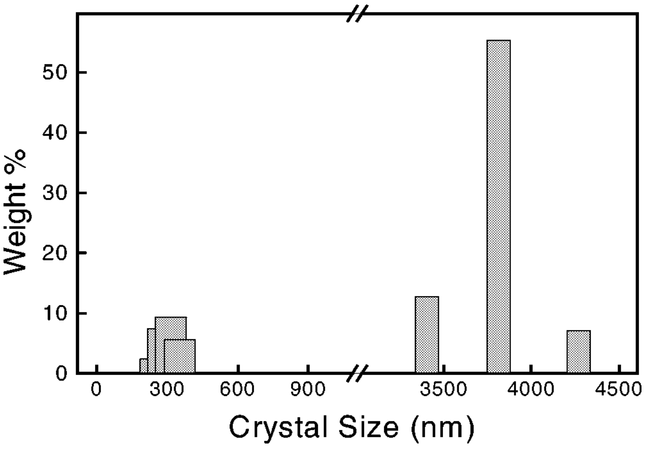

Figure 4. Crystal size distribution of sample synthesized by one-stage method at 170 °C.

solid product yield and the average crystal size, the crystal population can be calculated, as follows [17]:

$$N = \frac{6m}{\pi d^3 \rho}, \tag{1}$$

where N is the number of crystals per gram of zeolite, m the mass of zeolite, d the crystal diameter in cm, and ρ the density of FeZSM-5. It indicates that the crystal size is related to the crystal population N for a given system.

The product size distribution of FeZSM-5 is shown in figure 4. A bimodal size distribution was observed, indicating that secondary nucleation happened during the crystal growth. In other words, both nucleation and crystal growth take place simultaneously in the solution [19]. Thus, the crystal size of the ultimate product is determined by the ratio of the nucleation and crystal growth rates. The crystal growth rate increases more quickly than the nucleation rate with temperature [12]. Therefore, a lower synthesis temperature is favorable for the formation of a larger number of nuclei, resulting in a product with a smaller crystal size. This is consistent with the observation by Li et al. [17] in the synthesis of nanometer crystals of silicalite-1. However, low synthesis temperature leads to longer synthesis period and sometimes even to difficulty in obtaining the product. Padovan et al. [18] reported the synthesis of ZSM-5 at 120 °C for as long as 576 h under autogenous pressure. Other authors [20,21] also studied the synthesis of ZSM-5 at low temperatures (80–100 °C) under atmospheric pressure for about 8–10 days. These results suggest that the crystal growth rate of ZSM-5 was strongly dependent on the synthesis conditions, especially on the temperature.

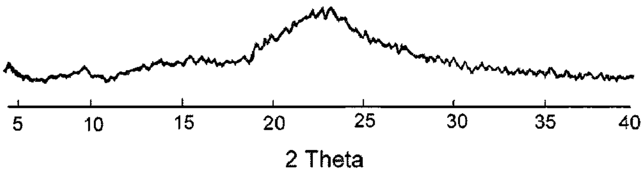

Figure 5. XRD pattern of a reaction mixture heated at 120 °C for 100 h.

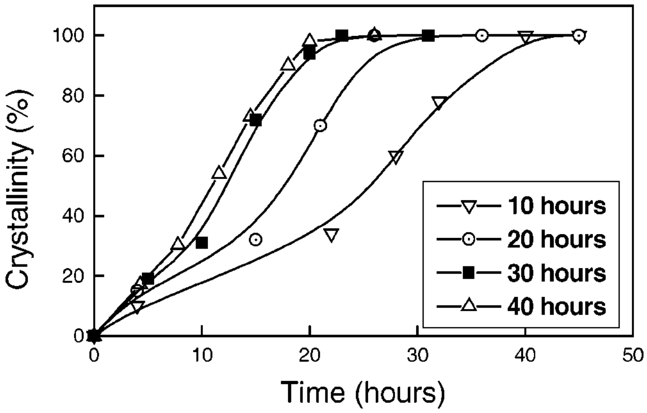

Figure 6. Crystallization curves of FeZSM-5 with different first-stage duration.

Figure 5 shows the XRD pattern of a reaction mixture after 100 h crystallization at 120 °C. No crystalline phase was detected, indicating that either no appreciable amount of crystalline material was formed or the crystal size is smaller than that detectable by XRD. Regev et al. [22] has observed spherical structure precursors (5 nm in size) of silica and alumina in a ZSM-5 synthesis mixture by cryo-TEM technique, while the same sample gave an amorphous pattern by wide-angle X-ray scattering. It is then concluded that the crystal growth rate (if any) was negligible at this temperature within the first 100 h, although a large amount of nuclei were formed. To this point, the nucleation rate was still unknown.

3.2. Two-stage varying-temperature synthesis

The two-stage synthesis was carried out according to the method described in section 2 with the hydrogel composition of $1SiO_2 : 0.02Fe_2O_3 : 0.6R : 0.3Na_2O : 50H_2O$ (R = n-butylamine). The reaction mixture was first kept at 120 °C for a certain period of time, and then abruptly raised to the required temperature (170 °C) for crystallization.

Figure 6 shows the crystallization curves of FeZSM-5 with different first-stage duration from 10 to 40 h. The

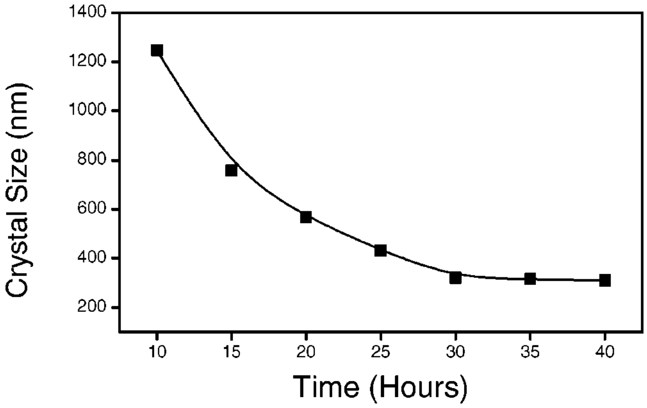

Figure 7. Influence of the first-stage nucleation on the final crystal size.

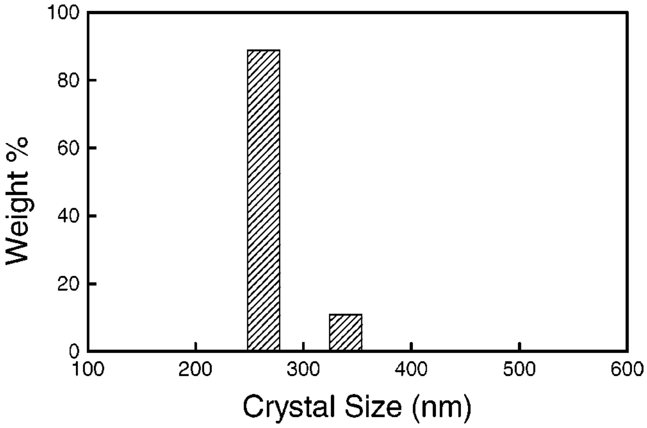

Figure 8. Crystal size distribution of sample synthesized by two-stage varying-temperature technique with the second-stage temperature of 170 °C.

time was recorded since the beginning of the second stage. It can be seen that the crystal growth occurred immediately once the temperature was raised after the low-temperature period at the first stage. Moreover, the longer the first-stage nucleation, the faster the crystallization, and the smaller the crystal of ultimate product achieved, as shown in figure 7, indicating a higher nucleus concentration in the reaction mixture. But the crystal size ceased decreasing after a certain period of low-temperature nucleation at the first stage, suggesting that the nucleus population had already reached the maximum. It is implied that the nucleation period for the synthesis of FeZSM-5 at 120 °C in this experiment was about 30 h.

Since the nucleation mainly took place at the first stage and a large number of nuclei formed in this period, it seems that the secondary nucleation was suppressed by the crystal growth at the second stage. This is not surprising because the crystal growth rate is independent of the nucleus size [23]; as there is a large amount of nuclei in the solution, fast crystal growth rate is expected. Hence, the nutrient in the reaction mixture was quickly consumed resulting in a sharp drop in supersaturation (s), which is defined as the ratio of the actual concentration to the normal equilibrium concentration ($s = c/c^*$) of silica and alumina in solution.

Figure 9. Scanning electron micrograph of sample prepared by two-stage method.

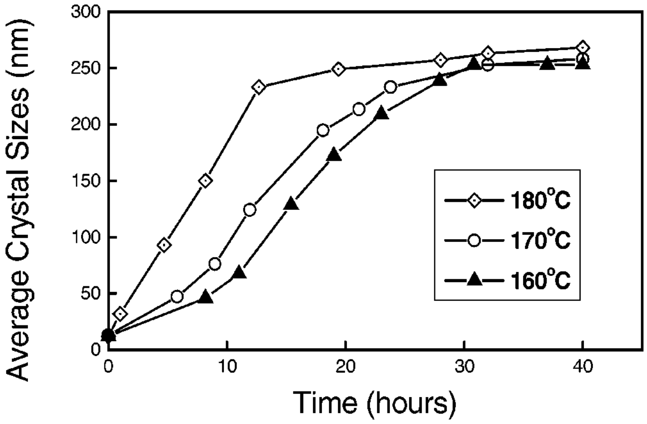

Figure 10. Relationship between final crystal size and the second-stage temperature.

Once the supersaturation is under the critical value, no nucleation will occur anymore. The crystal size distribution of the ultimate product is shown in figure 8. Besides the main peak, which accounts for ca. 90 wt%, another small peak appeared at about 320 nm. This result was also observed visually in the SEM photo presented in figure 9.

3.3. Effect of the second-stage temperature

The relationship between the crystal size of the ultimate product and the second-stage temperature is shown in figure 10. All the synthesis was carried out according to a procedure involving a first stage (120 °C) of 30 h and a second stage (160–180 °C) of more than 40 h. The hydrogel composition was the same as in section 3.2. It can be found that for a sufficiently long period of the first-stage nucleation, the crystal size had little change with the increase of the second-stage temperature, however, the crystal growth rate was increased. This can be attributed to the fact that the nuclei population reached its maximum at the first stage after the sufficiently long period of nucleation (>30 h), thus

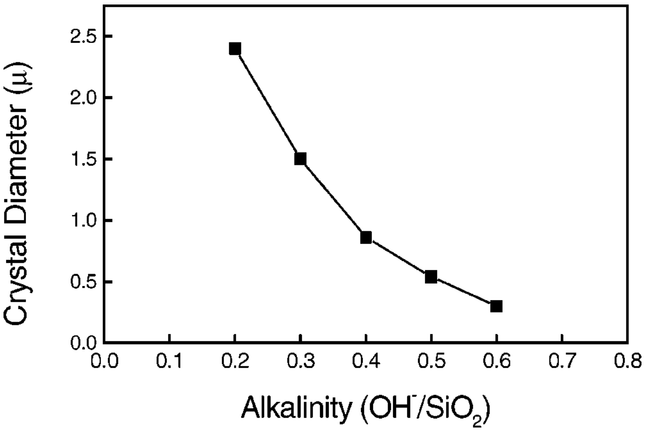

Figure 11. Influence of alkalinity on the average crystal size of the product in two-stage synthesis.

the temperature at the second stage only affected the crystal growth rate. This is in consistent with the observations by Li et al. [13].

3.4. Effect of alkalinity

The crystal size decreased with the increase of pH of the reaction system, as shown in figure 11. The chemical composition for the initial batches was $1SiO_2 : 0.02Fe_2O_3 : 0.6R : (0.1–0.3Na_2O) : 50H_2O$ (R $=$ n-butylamine). The synthesis procedure was the same as described in section 3.2. It is known that OH^-, usually referred to as alkalinity, can strongly increase the solubility of the gel phase in the mother liquid, leading to a higher supersaturation and smaller crystallite. Figure 11 shows the crystal size declines with increasing alkalinity in the range of $OH^-/SiO_2 = 0.2$–0.6. Further increase of the alkalinity led to the formation of α-SiO_2, due to the fact that the Fe-ZSM-5 is metastable under this condition and a more stable phase will appear.

3.5. Effect of template

The organic structure-directing agents have also influences on the final crystal size. Three kinds of template (n-butylamine, ethylenediamine and hexanediamine) were used, in place of the more expensive quaternary ammonium compounds usually used in the synthesis of ZSM-5. The starting gel composition was $1SiO_2 : 0.02Fe_2O_3 : 0.6R : 0.3Na_2O : 50H_2O$, and the procedure was the same as described in section 3.2, with the second-stage temperature of 180 °C. The crystal size of the ultimate product decreased in the order n-butylamine (300 nm) $<$ hexanediamine (340 nm) $<$ ethylenediamine (420 nm). The nucleation periods at 120 °C determined for systems containing n-butylamine, ethylenediamine and hexanediamine as templates were 30, 51 and 73 h, respectively. The nucleation and nucleation duration are different for different kinds of template, therefore, different amounts of nuclei exist and finally different sizes of crystallites are formed.

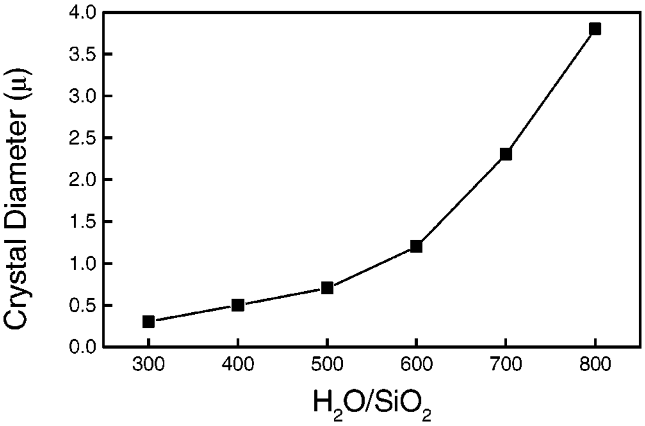

Figure 12. Influence of the sol concentration on the crystal size.

3.6. Effect of sol concentration

Figure 12 shows the influence of the sol concentration on the crystal size. The reaction mixture compositions for these runs were $1SiO_2 : 0.02Fe_2O_3 : 0.6R : X Na_2O : (50–200)H_2O$ with R $=$ n-butylamine and performed according to the same procedure, as described in section 3.3. The pH is kept at 13 for all runs to ensure the same solubility of the amorphous gel. As can be seen, when the water content was reduced, the crystallization rate increased and the crystal size decreased under the conditions employed. This can again be explained in term of the supersaturation increase. When reducing the water content in the hydrogel, the supersaturation increases and hence more nuclei are produced, leading to smaller crystallite. It is worth noting that further reduction of water content leads to a contrary effect. This is probably due to an increase in the reaction mixture viscosity decreasing the mass transfer rate in the liquid phase [24].

4. Conclusions

Small crystal FeZSM-5 (ca. 300 nm) was synthesized by a two-stage varying-temperature technique, in which the reaction mixture was first kept at a relatively low temperature (120 °C) to ensure the largest nuclei population, then the temperature was swiftly raised to a higher value to achieve the fast crystal growth rate. It was found that the crystal size decreased with increasing first-stage duration and reached the minimum after the completion of nucleation. The second-stage temperature had no significant influence on the crystal size but mainly altered the crystal growth rate provided that the first-stage duration was long enough. The crystal size decreased under elevated alkalinity and reduced water content in the hydrogel due to the increase in liquid supersaturation. The templates also influenced the crystal size by changing the nucleation rate in the first-stage and in turn the nucleus population at the beginning of the second stage.

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