Evolution of Aggregate-Like ZSM-5 Crystals

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Abstract—A series of zeolites ZSM-5 has been synthesized in hydrothermal conditions at 160°C by varying the time of HT treatment with the following molar compositions of the precursor gel: 1.0 SiO\textsubscript{2} : 0.01 Al\textsubscript{2}O\textsubscript{3} : 0.2 TPAOH : 0.05 Na\textsubscript{2}O : 50 H\textsubscript{2}O : 4.0 EtOH. Materials have been characterized by X-ray diffraction, transmission electron microscopy and nitrogen adsorption measurements. We have succeeded to synthesize ZSM-5 crystals with metastable aggregate-like morphology reproducibly and to follow their evolution during HT treatment.

Keywords: zeolite, ZSM-5, crystallization, morphology

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Zeolites are crystalline microporous aluminosilicates widely used as high-performance adsorbents and heterogeneous catalysts in different fields such as refining, petrochemistry and fine chemicals industries owing to integrating “molecular sieve” properties, flexible chemical composition and outstanding thermal and hydrothermal stability [1, 2]. Size and shape of zeolite crystals directly influencing the reactant and product diffusivities should be precisely tuned to provide the efficiency of given adsorbent/catalyst [3, 4]. Key factors controlling the size and morphology of zeolite crystals are the precursor composition, temperature and duration of aging/hydrothermal treatment [5–10].

Catalysts, containing zeolite ZSM-5, are widely used in refining and petrochemistry, however in most reactions, particularly involving large molecules, traditionally used micron-sized crystals promote low catalyst utilization and fast deactivation. To increase zeolite utilization, there are two main approaches: decreasing the diffusion path by reducing the size of the crystals and increasing the effective diffusion coefficient by introducing additional mesopores in the crystal structure. In our previous work mesoporous crystals with aggregate-like morphology were observed under the varying dilution of the gel with molar ratio 1.0 SiO\textsubscript{2} : 0.01 Al\textsubscript{2}O\textsubscript{3} : 0.2 TPAOH : 0.05 Na\textsubscript{2}O : xH\textsubscript{2}O : 4.0 EtOH, where \(x \approx 10–300\) [11]. The morphology of ZSM-5 crystals was shown to depend on the dilution of precursor solution: both the most concentrated and the most diluted precursor solutions with H\textsubscript{2}O/SiO\textsubscript{2} = 10 and 300, respectively, resulted in producing compact “rounded-boat” crystals, while zeolite materials synthesized from mixtures with H\textsubscript{2}O/SiO\textsubscript{2} = 25–100 represented aggregate-like ellipsoid crystals.

Here we present new experimental data showing the evolution of ZSM-5 crystals from precursor solutions with H\textsubscript{2}O/SiO\textsubscript{2} = 50 during 168 h of hydrothermal (HT) treatment. It was shown how time of HT treatment impact on product yield, crystallinity, crystal size, morphology and texture of ZSM-5 crystals.

EXPERIMENTAL

Materials. Tetraethylorthosilicate (TEOS, 98 wt %, Angara reactive), tetrapropylammonium hydroxide (TPAOH, 25 wt % solution in water, Acros), NaOH (98 wt %, Tellura) and aluminium isopropoxide (AIP, Acros) were applied for the zeolite syntheses.

Synthesis. A series of zeolite ZSM-5 samples were synthesized in hydrothermal conditions by varying the time of HT treatment with the following molar compositions: 1.0 SiO\textsubscript{2} : 0.01 Al\textsubscript{2}O\textsubscript{3} : 0.2 TPAOH : 0.05 Na\textsubscript{2}O : 50 H\textsubscript{2}O : 4.0 EtOH.
0.05 Na$_2$O : 50 H$_2$O : 4.0 EtOH. A typical synthesis was carried out as follows. 0.14 g of AIP was dissolved in 1.4 mL of TPAOH under vigorous stirring for 2 h to obtain a clear aluminohsilicate solution. 0.13 g of NaOH was dissolved in a mixture of 28.4 mL of distilled water and 4.0 mL of TPAOH, and then 7.5 mL of TEOS was added dropwise. After stirring for 15 min, aluminohsilicate solution was added dropwise, the mixture was stirred for 24 h. The resultant mixture was placed in a Teflon-lined stainless steel autoclave and subjected to the hydrothermal treatment in an oven at 160°C for required time from 2 to 168 h. The product was purified in a series of three steps consisting of centrifugation at a relative acceleration 1500 g for 5 h, followed by removal of mother liquor and redispersion in distilled water under ultrasonication, and then the procedure was repeated several times until pH of the suspension reached 7. Purified product was dried at 373 K for 12 h and then calcined by linear heating up to 823 K for 2 h and maintaining at 823 K for 4 h. The product yield was calculated by dividing the mass of the calcined zeolite obtained by the theoretical one and multiplying by 100%.

Specific surface areas were determined applying BET equation [12]. Micropore volume and external surface area (the surface area of pores larger than micropores) were calculated by means of $\alpha_s$-method [13] using the isotherm of adsorption of N$_2$ on the reference LiChrospher Si-1000 silica gel, reported in the literature [14], the range of $\alpha_s$ from 0.5 to 0.8 was used. Nitrogen adsorption-desorption isotherms and TEM images were obtained for selected number of samples enough to observe the changing texture and morphology during hydrothermal synthesis.

**RESULTS AND DISCUSSION**

XRD patterns of calcined samples of zeolite ZSM-5 synthesized by varying the time of HT treatment and the reference one [15] are shown in Fig. 1, ranges of 20 for the most intensive peaks (7°–10° and 22.5°–25.0°) are increased and placed separately on the right. Location of the peaks of synthesized zeolites coincide with those of the reference MFI structure. XRD of calcined ZSM-5 zeolite from the database http://www.iza-structure.org/ databases/ was used as a reference. The peaks referred to synthesized zeolites are broadened and some of them are overlapped resulting from both decreasing coherent scattering region and instrumental broadening (Table 1).

We evaluated the relative crystallinity by the area of the peaks in the range from 22.5 to 25.0 (Table 2). It should be noted, that for the correct estimation of relative crystallinity XRD patterns were obtained under the same recording conditions and the same mass of samples (0.2 g). The crystallinity has a trend to grow while

| $h$ | $k$ | $l$ | 20, deg (calculated for MFI structure) | Average 20, deg (synthesized zeolites) |
|-----|-----|-----|--------------------------------------|--------------------------------------|
| −1  | 0   | 1   | 7.93                                 | 7.95                                 |
| 0   | 1   | 0   | 7.94                                 |                                       |
| 1   | 0   | 1   | 8.01                                 |                                       |
| 2   | 0   | 0   | 8.80                                 |                                       |
| −1  | 1   | 1   | 9.07                                 | 9.09                                 |
| 1   | 1   | 1   | 9.14                                 |                                       |
| −5  | 0   | 1   | 23.27                                | 23.3                                 |
| 5   | 0   | 1   | 23.42                                |                                       |
| −5  | 1   | 1   | 23.69                                | 23.75                                |
| 5   | 1   | 1   | 23.84                                |                                       |
| −3  | 1   | 3   | 24.35                                | 24.45                                |
| 3   | 1   | 3   | 24.61                                |                                       |
prolonging HT treatment up to 51 h and then to fall during the following 118 h (Table 2).

The average yield of zeolites synthesized during more than 5.5 h was 87±2%, while the yield of the sample subjected to HT treatment for 3 h was only 39%. We also succeeded to separate a negligible amount of the sample prepared for 2 h of HT treatment with yield less than 1%, being sufficient only for TEM analysis.

TEM images of zeolite materials prepared during different time of HT treatment from 2 to 168 h are presented in Fig. 2. We have estimated the average crystal size of zeolite crystals by measuring size of 100 particles at a number of TEM images (Fig. 3). Monodisperse MFI crystals with the average size of 50 nm uniformly distributed inside the amorphous phase are observed in TEM images of the sample subjected to HT treatment for 2 h. The data obtained indicates that the nucleation and initial crystal growth of zeolite from our mixture with molar ratio 1.0 SiO₂ : 0.01 Al₂O₃ : 0.2 TPAOH : 0.05 Na₂O : 50 H₂O : 4.0 EtOH most likely occurs in the gel matrix through the reorganization of solid amorphous material due to dissolution – condensation processes [16]. After 3 h of HT treatment the average crystal size increased up to 230 nm, the crystal surface

Table 2. Characteristics of ZSM-5 samples, synthesized from precursor solutions with different H₂O/SiO₂ molar ratios

| Sample (HT time) | XRD crystallinity, % | Yield, % |
|------------------|----------------------|----------|
| 2                | –                    | <1       |
| 3                | 82                   | 39       |
| 5.5              | 91                   | 86       |
| 15               | 98                   | 90       |
| 27               | 97                   | 86       |
| 39               | 87                   | 86       |
| 51               | 100                  | 84       |
| 72               | 93                   | 89       |
| 88               | 93                   | 85       |
| 96               | 78                   | 78       |
| 168              | 69                   | 87       |

Fig. 1. XRD patterns of calcined ZSM-5 samples synthesized during different time of HT treatment.
Fig. 2. TEM images of calcined ZSM-5 samples synthesized for different time of HT treatment.
became rougher. It should be noted, that amorphous phase was not observed in TEM images in the case of the sample synthesized for 3 h, yield of solid product being is only 39% and XRD crystallinity is 82%. It means that the amorphous gel either lost stability and decomposed into nanoparticles, which were not separated by centrifugation, or totally dissolved under the consumption of silicate species during the crystallization process. The following evolution of ZSM-5 crystals during HT treatment associated both with growing the crystal size and significant modification of the crystal morphology. Zeolite crystals turned into aggregate-like ellipsoid crystals with the average size of 300 nm after 15 h of HT treatment. The average sizes of domains forming aggregate-like crystals are in the range of 30–50 nm. Aggregate-like crystals appeared to be generated by the attachment of the solid precursor domains on the zeolite surface followed by their transformation into MFI phase via dissolution—condensation steps resulting in the formation of inseparable parallel planes across each crystal. A mechanism where the precursor 5-nm building units evolve to silicalite-1 crystals through aggregative growth was earlier shown here [17]. Further evolution of aggregate-like ZSM-5 crystals under HT treatment represent both increasing the average crystal size and gradual smoothing the surface of zeolite crystals because of Ostwald ripening. Moreover, the transition into thermodynamically stable “rounded-boat” morphology was observed resulting from the crystal reconstruction driven by the minimization of surface free energy.

Significantly, zeolite yield after 15 h of HT treatment remains approximately constant indicating evolution of aggregate-like crystals proceed precisely through the reconstruction of those. Thereby, ZSM-5 crystals with aggregate-like morphology turned out to be metastable and we have succeeded to reproducibly synthesize them.

Before discussing textural characteristics of synthesized ZSM-5 samples peculiarities of application of BET equation to evaluate the surface area of zeolites should be considered. Bae and coauthors shown that choice of appropriate pressure range based on consistency criteria allows obtaining surface areas from \( N_2 \) adsorption-desorption data being in good agreement with those obtained directly from crystal structures [18]. Here we have used two consistency criteria suggested by Rouquerol et al. [19] and recommended by IUPAC [20] to obtain the BET surface areas from the linear region of nitrogen isotherms: (a) the quantity \( C \) should be positive; (b) application of the BET equation should be restricted to the range where the term \( V(1 – P/P_0) \) continuously increases with \( P/P_0 \), where \( V \) is the volume of nitrogen adsorbed per gram of material. Therefore, \( P/P_0 \) range for approximation of experimental data by BET equation was chosen from 0.001 to 0.01.

All zeolite samples exhibit high BET surface areas (470–590 m²/g) and micropore volumes (0.14–0.19 cm³/g). The effect of time of HT treatment on textural characteristics of ZSM-5 samples is shown in Fig. 4. The reduction of the BET surface area and micropore volume after 72 h of HT treatment is in accordance with falling their XRD crystallinity. External surface area (the surface area of pores larger than micropores) was simultaneously increased, indicating mesopore formation because of partial destruction of zeolite lattice. Falling the total pore of the zeolite sample during HT treatment took place in two steps. The first step after 3 h of HT treatment appeared to result from decreasing the contribution of mesopore volume between packed crystals, and the second one after 72 h—because of smoothing the surface of zeolite crystals.

CONCLUSIONS

We have succeeded to synthesize ZSM-5 crystals with metastable aggregate-like morphology reproducibly from the mixture with molar ratio 1.0 SiO₂ : 0.01 Al₂O₃ : 0.2 TPAOH : 0.05 Na₂O : 50 H₂O : 4.0 EtOH at 160°C and to observe their evolution during HT treatment. The evolution of ZSM-5 crystals during HT treatment

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**Fig. 3.** The dependence of average crystal size of zeolite ZSM-5 on time of HT treatment.
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associated both with growing the crystal size and significant modification of the crystal morphology. Initially, monodisperse MFI crystals with the average size of 50 nm uniformly distributed inside the amorphous phase formed during 2 h of HT treatment. Then nanocrystals located in the gel matrix transform to rough crystals with the size about 200–250 nm, followed by 300 nm ellipsoid aggregate-like crystals generation with their gradual smoothing and transiting into thermodynamically stable “rounded-boat” morphology. While smoothing and faceting the crystals both decreasing the XRD crystallinity, micropore volume and increasing the external surface area (the surface area of pores larger than micropores) of zeolite crystals have been observed resulting from the partial destruction of the zeolite lattice under prolonged hydrothermal treatment in alkaline medium.

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CONFLICT OF INTEREST

The authors declare no conflict of interest requiring disclosure in this article.

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Fig. 4. The effect of time of HT treatment on textural characteristics of ZSM-5 samples: BET and mesopore surface area (a); total and micropore volume (b).
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