J Mater Sci (2009) 44:3777–3783
DOI 10.1007/s10853-009-3508-6

In situ assembly of ZSM-5 nanocrystals into micro-sized single-crystal-like aggregates via acid-catalyzed hydrolysis of tetraethylorthosilicate

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Received: 17 January 2009 / Accepted: 20 April 2009 / Published online: 11 May 2009

Abstract ZSM-5 aggregates were synthesized with the silica source tetraethylorthosilicate (TEOS) being hydrolyzed at acidic conditions to produce siliceous precursors, followed by the addition of aluminum sulfate and tetrapropyl ammonium bromide (TPABr), and with the resulting gel mixture being hydrothermally crystallized at basic conditions. The obtained products were characterized by XRD, SEM, and N_2 adsorption. Well crystallized ZSM-5 can be successfully synthesized through the sulfuric acid-catalyzed hydrolysis of TEOS within a short crystallization time 35 h. The thus produced micro-sized single-crystal-like zeolite ZSM-5 aggregates (10 μm) are made of uniformly distributed nanocrystals with sizes of about 200 nm. Moreover, by adjusting the hydrothermal reaction parameters, such as increasing the crystallization temperature, the $TPABr/SiO_2$ ratio and the pH value of reaction solution, the crystallization is accelerated substantially. Also, the moderate H_2O/SiO_2 molar ratio of 20–60 in the synthesis mixture can lead to pure ZSM-5, and yet the optimal ratio is 40.

Introduction

Since Mobil first reported the synthesis of ZSM-5 in 1972 [1], it has been attracting great attention because of its catalytic applications in oil refinery, petro-chemical industry, and environmental protection [2–5]. During the last decade, a lot of efforts have been devoted to the preparation of small sized crystals of ZSM-5 zeolite due to its higher external surface area and more exposed active site, as well as the reduction of diffusion pathway for molecules in catalysis [6–8]. Moreover, they are still being developed for new applications in optics [9], membranes [10], and sensors [11].

The dissolution of silica precursors is one of the most important factors for the synthesis of zeolite, through which the silicate intermediates are formed followed by the onset of nucleation and crystallization [12]. Thus, the silica source largely influences the morphology and crystal size of a zeolite [13]. Although various silica sources, typically including water glass, fumed silica, TEOS, colloidal silica, and sodium metasilicate, have been used for the synthesis of ZSM-5 [11, 14–16], TEOS is still the most commonly employed silica source for the synthesis of small crystal ZSM-5 because it favors to cause the homogeneity for a starting synthesis system. Griken et al. [17] synthesized ZSM-5 with crystal sizes of 10 ∼ 100 nm at autogenous pressure starting from TEOS-derivated clear solutions. Aguado et al. [18] obtained the ultra-small crystal size (10–200 nm) of ZSM-5 with TEOS as silica source at a low crystallization temperature under atmospheric pressure. Mohamed et al. [13] revealed that TEOS resulted in a smaller average crystal size of ZSM-5 than colloidal silica did. Via the two-stage varying-temperature procedure, Li et al. [19, 20] observed a smaller nano-sized silicalite-1 from TEOS (63 nm) than those from Ludox TM (160 nm) and Ludox LS (169 nm), and they also stated that the nucleation was faster in the former case. However, using the above methods, only when the SiO_2/Al_2O_3 ratio was high or without alumina, could the nano-sized MFI zeolites be formed [11].

Electronic supplementary material The online version of this article (doi:10.1007/s10853-009-3508-6) contains supplementary material, which is available to authorized users.

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It is known that the silica and alumina species in a synthesis mixture are crystallized into zeolite structures only at strong basic conditions [21]. Hence, the pioneering investigators, succeeding in the synthesis of small sized ZSM-5, always hydrolyzed TEOS in a basic medium for obtaining silica precursors. In fact, TEOS can be catalytically hydrolyzed at acidic conditions, nevertheless, thus produced silica precursors are different from the base-catalyzed ones [22]. Recently, our group found that zeolite MCM-22 can be rapidly obtained by acid-catalyzed hydrolysis of TEOS [23, 24]. However, at the best of our knowledge, the synthesis of small-sized ZSM-5 via the hydrolysis of TEOS in a strong acid medium has not been reported as yet.

In this study, we report in detail the facile synthesis of the small-sized ZSM-5 that is aggregated into micro-sized particles with low SiO_2/Al_2O_3 ratio using TEOS as the silica source, aluminium sulphate as the aluminium source, and the inexpensive TPABr as the structure-directing agent (SDA). The novelty of this method is to hydrolyze TEOS in a strong acid medium to produce silica precursors, which is used as the real silica source, and the synthesis mixture is adjusted into a strong basic mixture just before the onset of crystallization. Various synthesis parameters are investigated to give the optional synthesis conditions.

Experimental

Synthesis

The following is a typical synthesis procedure. A total of 10.0 g TEOS was mixed with 32.5 g deionized water in a beaker. Under vigorous stirring, sulphuric acid (or aqueous solution of sodium hydroxide) was slowly dropped into the TEOS solution to obtain a pH value of 1.0 (or 10). The obtained mixture was stirred at 20 °C for 20 h to get a complete hydrolysis of TEOS. Then, 1.2 g TPABr and 0.75 g $Al_2(SO_4)_3 \cdot 18H_2O$ were introduced into the above mixture with stirring at room temperature for 10 min, followed immediately with the pH value regulation into 10 by NaOH with the formation of a hydro-gel at the basic condition. Finally, the slurry was transferred to a Teflon-lined stainless steel autoclave and left to crystallize statically at 180 °C. The final composition of the gel was: $0.22Na_2O$: SiO_2: $0.025Al_2O_3$: 0.1TPABr: $40H_2O$. Products from the synthesis were separated by centrifugation, washed with deionized water and air-dried at 100 °C. The obtained as-synthesized samples were calcined at 550 °C for 5 h in air stream to give the as-calcined ZSM-5.

Characterization

The products were characterized by X-ray powder diffraction (XRD, Bruker D8 ADVANCE diffractometer with Cu Kα radiation, $\lambda = 0.1542$ nm, 40 kV, 20 mA), scanning electron microscopy (SEM, FEI QUANTA 200), brunauer ammett teller (BET, Micromeritics ASAP2010), and inductively coupling plasma (ICP, Jarrell-Ash 1100).

Results and discussion

Effect of various catalysts for the hydrolysis of TEOS

XRD patterns for the samples obtained by the hydrolysis of TEOS with different catalysts are illustrated in Fig. 1. It can be seen that sulfuric acid-catalyzed hydrolysis of TEOS resulted in a well resolved curve matching well with that of the MFI topology with only 35 h of crystallization time. However, when the hydrolysis of TEOS was carried out in aqueous solution of NaOH, low-intense Bragg reflections of MFI zeolite were detected even with a longer crystallization time of 60 h. Furthermore, without any catalysts for the hydrolysis of TEOS, the same synthesis caused barely an amorphous phase.

The previous report [25] showed that polymers formed under acid-catalyzed conditions for the hydrolysis of TEOS were highly overlapped or entangled prior to gelation, while polymers formed under base-catalyzed conditions did not

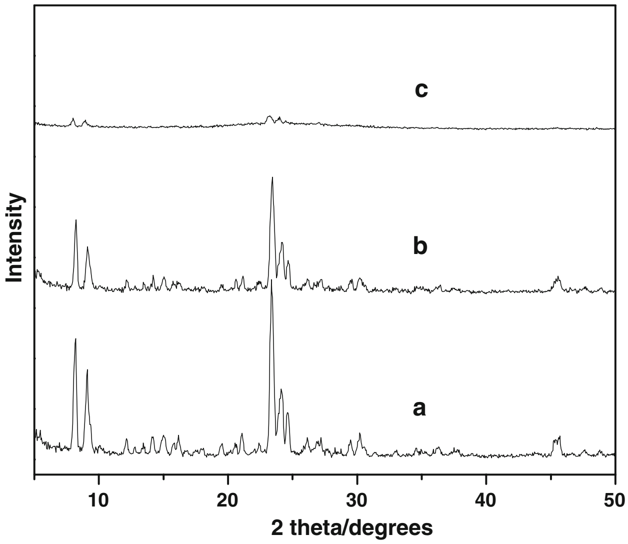

Fig. 1 XRD patterns for as-calcined samples obtained via the hydrolysis of TEOS by different catalysts with the gel composition SiO_2:$0.025Al_2O_3$:0.1TPABr: $40H_2O$ at the crystallization temperature 180 °C. (*a*) H_2SO_4, with 35 h of crystallization time; (*b*) NaOH, with 60 h of crystallization time; (*c*) without catalyst, with 60 h of crystallization time

interpenetrate and thus behaved as discrete clusters. The clear difference between the acid- and base-catalyzed hydrolysis of TEOS was also investigated by Sanchez et al. [26] and Šefčík et al. [27], revealing that hydrolysis is the rate-limiting step at basic conditions whereas condensation is rate-limiting at acid conditions, which cause the formation of larger particles at former conditions and small cage-like units in later case. Therefore, from the observations in Fig. 1, one can reasonably draw that the very different synthesis results should associate closely with the different silica precursors generated from the hydrolysis of TEOS catalyzed under acid or base conditions, and the silica precursors arising from the sulfuric acid-catalyzed hydrolysis of TEOS much favor to the formation of ZSM-5 crystal.

Other than sulfuric acid, crystallization curves for the synthesis of ZSM-5 via various acid-catalyzed hydrolyses of TEOS are compared in Fig. 2. It can be seen that using sulfuric acid as the catalyst for the hydrolysis of TEOS, the highest crystallization rate was obtained, allowing a 100% crystallinity of ZSM-5 (BET surface area: 361 m^2/g, Al_2O_3/SiO_2 molar ratio: 27) with a short crystallization time 35 h. Hydrochloric acid-catalyzed hydrolysis of TEOS could also make pure ZSM-5 (BET surface area: 350 m^2/g) but with a longer crystallization time 55 h. With nitric acid and phosphoric acid as the catalysts, ZSM-5 zeolite was produced with 90 and 80% crystallinity after 55 and 60 h, respectively. In contrast, for the basic (NaOH) catalyst, ZSM-5 zeolite was obtained with only 60% crystallinity after 60 h.

Figure 3 displays SEM images for the samples obtained via the hydrolysis of TEOS with acid or base catalysts. From Fig. 3a, it can be seen that the sample synthesized by sulfuric acid-catalyzed hydrolysis of TEOS consisted of single-crystal-like spherical micro-sized particles with the diameter about 10 μm. A high-magnification view in Fig. 3b showed that the micro-sized particles were aggregates assembled by the small crystals with shapes of cubic prisms. It could be clearly observed in the top view for the surface of an aggregate in Fig. 3c that such single-crystal-like particles were made of uniformly distributed nanosized crystals with a size of about 200 nm. No significant differences in the SEM images for zeolite assemblies obtained by hydrolyzing TEOS in solutions of sulfuric acid, nitric acid, and phosphoric acid can be observed.

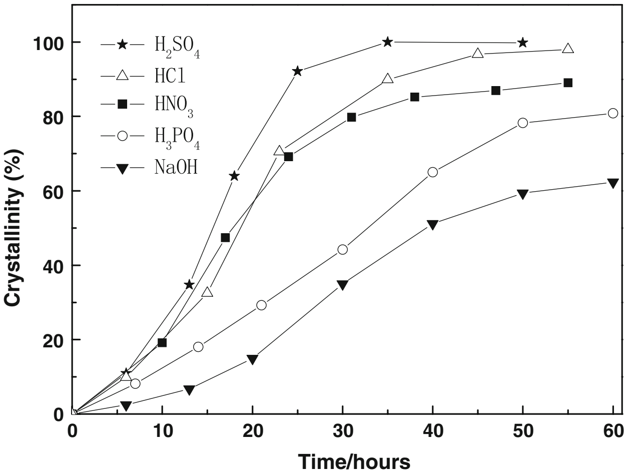

Fig. 2 Crystallization curves for as-calcined samples synthesized by using different catalysts for the hydrolysis of TEOS at the crystallization temperature of 180 °C with the gel composition SiO_2: $0.025Al_2O_3$:0.1TPABr:$40H_2O$

The formation of the special single-crystal-like spherical morphology may be understandable by the mechanism of aggregation–densification–zeolititation proposed by Serrano et al. [28]. It is inferred that in the early stage of the crystallization process, the primary units are built up via the inorganic–organic composites [29]. Then, nucleation takes place within the primary units of the amorphous solid, which is proposed to be the parent of the final single-crystal-like aggregate. The nuclei rapidly grow and cause the formation of numerous nanocrystals until the surrounding nutrients are used up. The nanocrystal possesses more or less the similar crystal size due to the equilibrium between the nuclei and nutrias. Along with this process, the nanocrystals assembled together to form a micro-sized particle.

For comparison, the image of ZSM-5 in Fig. 3d obtained through the sodium hydroxide-catalyzed hydrolysis of TEOS gave the tablet-like ZSM-5 crystals with the size of about 2 μm, which is commonly seen in many previous reports [13, 30].

Effect of crystallization temperature

It is well established that the crystallization temperature significantly influences the nucleation and crystal growth in the synthesis of zeolite [31]. In this work, the crystallization temperature was changed from 120 °C to 200 °C for the same synthesis mixture SiO_2: $0.025Al_2O_3$: 0.1TPABr: $40H_2O$, which was prepared by sulfuric acid-catalyzed hydrolysis of TEOS, and the corresponding crystallization curves are displayed in Fig. 4. It can be seen that, when the crystallization temperature was 120 °C, only amorphous phase was observed, and with the increase of temperature to 150 °C, the crystallinity of the obtained ZSM-5 product was 70% without detecting other crystal phases after 60 h. The further increase of the temperature up to 180 °C led to a large reduction of crystallization period to 35 h with a ZSM-5 crystallinity of 100%. Consequently, the crystallization period decreased substantially with increasing the crystallization temperature. This tendency is quite well in agreement with the previous result that the increasing of temperature can accelerate the solubility of silicate species,

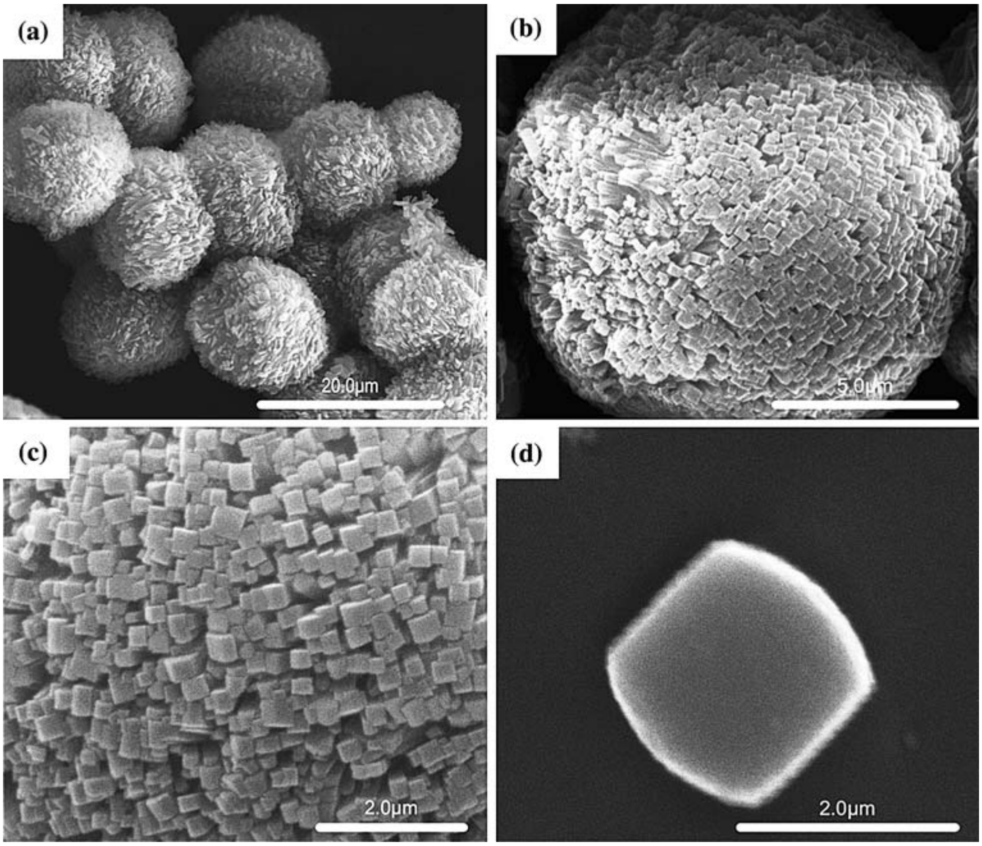

Fig. 3 SEM images for as-calcined samples obtained by using different catalysts for the hydrolysis of TEOS at the crystallization temperature of 180 °C with the gel composition SiO_2:0.025Al_2O_3:0.1 TPABr:40H_2O. **a**–**c** H_2SO_4, crystallization time 35 h; **d** NaOH, crystallization time 60 h. The scale bars are: (**a**) 20 μm, (**b**) 5 μm, (**c**) and (**d**) 2.0 μm

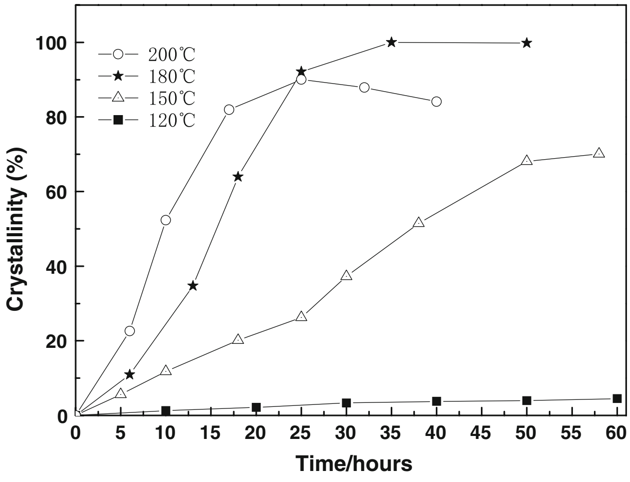

Fig. 4 Crystallization curves for as-calcined samples synthesized at different crystallization temperatures via sulfuric acid-catalyzed hydrolyses of TEOS with the gel composition SiO_2:0.025Al_2O_3:0.1TPABr:40H_2O

leading to the rapid growth of ZSM-5 crystals [31, 32]. Nevertheless, at a much high crystallization temperature of 200 °C, the ZSM-5 crystallinity of the product decreased to 90% at the optimal crystallization time of 25 h, and moreover, quartz was detected in final product due to the high temperature. Hence, 180 °C is selected as the preferred crystallization temperature for the transformation of the amorphous gel mixture into ZSM-5 zeolitic phase.

The morphology of samples synthesized at various crystallization temperatures with the crystallization time of 35 h are shown in Fig. 5. At 120 °C, the product was clearly amorphous (Fig. 5a). By increasing the temperature to 150 °C, particles consisting of preliminary crystallites appeared (Fig. 5b). When the temperature increased to 180 °C, the crystal size of ZSM-5 was around 200 nm that aggregated into micro-sized particles (Figs. 5c and 3a). The morphology of the sample obtained at the crystallization temperature of 200 °C was similar to that at 180 °C, except that the crystal size in former case was larger than that in the later case (Fig. 5d).

Influence of the TPABr/SiO_2 ratio

Templates play a significant role in the synthesis of zeolite due to its capability to alter the chemistry of the gel [33, 34] and to direct the typical oligomers into a specific framework [35, 36]. Thus, the control of the type and

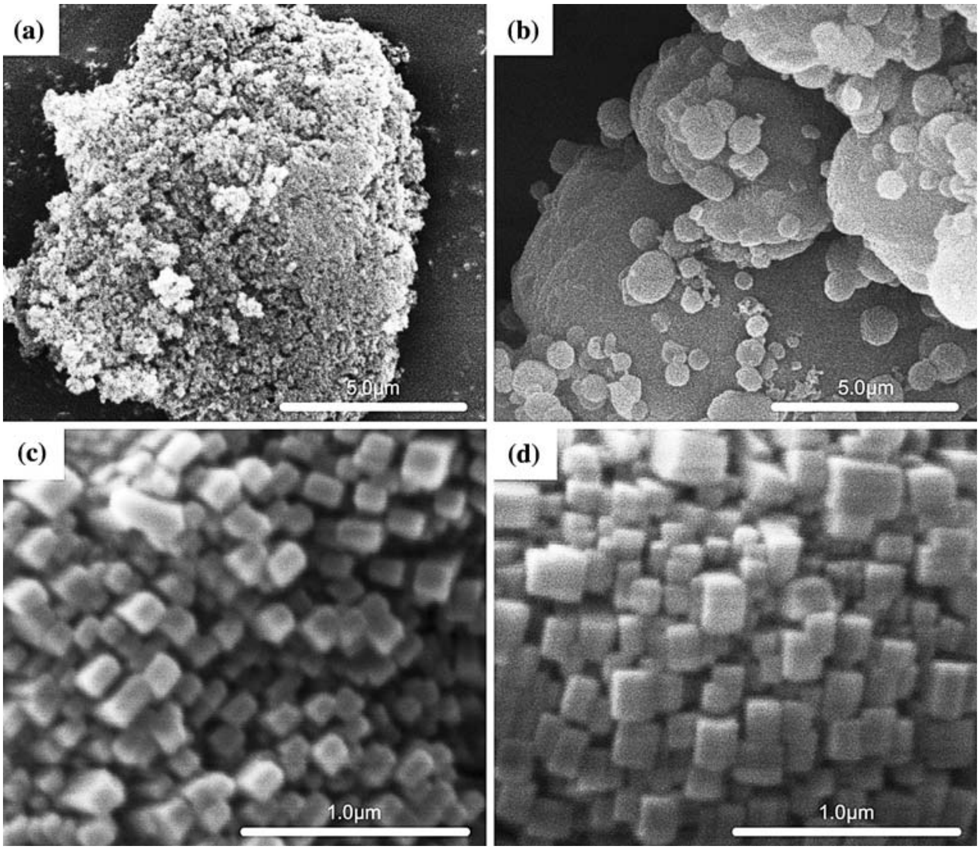

Fig. 5 SEM images for samples synthesized at different crystallization temperatures after 35 h via the hydrolysis of TEOS by sulfuric acid with the gel composition SiO_2:$0.025Al_2O_3$:0.1TPABr:$40H_2O$. **a** 120 °C, **b** 150 °C, **c** 180 °C, and **d** 200 °C. The scale bars are: **a** and **b** 5 μm, **c** and **d** 1 μm

amount of templates in zeolitization process is very important. It is well known that tetrapropylammonium hydroxide (TPAOH) is wildly used as the template for the synthesis of ZSM-5 [2, 37, 38]. However, TPAOH is too expensive to apply for large-scaled production of ZSM-5. In this work, we take TPABr, which is much cheaper than TPAOH, as the template in the synthesis system via acid-catalyzed hydrolysis of TEOS. In order to investigate the effect of template content, the template/silica molar ratios were changed from 0 to 0.1 in the synthesis of ZSM-5, and the XRD patterns and SEM images for the as-calcined samples are shown in Figs. 6 and 7. It can be seen from the curve of Fig. 6a and Fig. 7a that only amorphous gel was obtained for the sample synthesized without any templates. However, pure ZSM-5 occurred when using TPABr as template (Curves of Fig. 6b, c), and intensities of the featured peaks assigned to ZSM-5 zeolite phase remarkably jumped with the increase of the TPABr content. The morphology of the final products obtained at 0.05 TPABr/SiO_2 molar ratio was spherical particles with a smooth surface and a particle size around 15 μm (Fig. 7b). This particle had a set of very weak XRD peaks for ZSM-5 (Curve of Fig. 6b), which implies that in this particle there exist many not well crystallized ZSM-5 nanocrystals, among which, the left nutrients are ready to be consumed if longer crystallization time is given. When the molar ratio of TPABr/SiO_2 increased to 0.1, small sized well crystallized ZSM-5 crystals of about 200 nm were clearly observed, and the small crystals assemble well to each other mostly because they originate from a same parent particle. The further increasing of the TPABr/SiO_2 molar

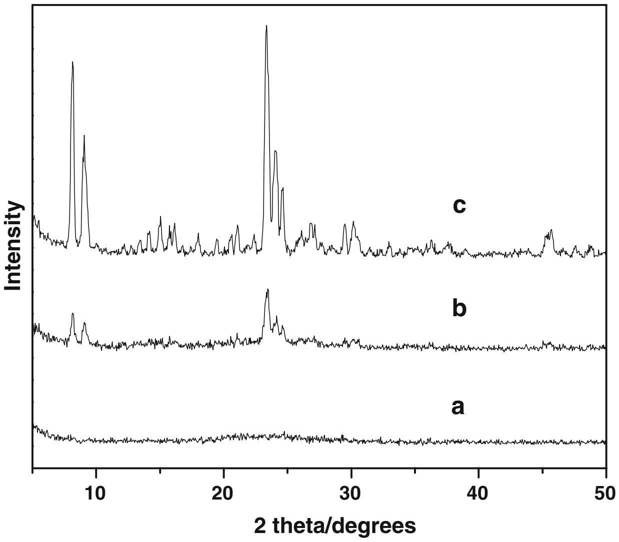

Fig. 6 XRD patterns of as-calcined samples obtained from SiO_2:$0.025Al_2O_3$:xTPABr:$40H_2O$ via sulfuric acid-catalyzed hydrolysis of TEOS with the crystallization time of 35 h at 180 °C. TPABr/SiO_2 ratios x are: (*a*) 0.00, (*b*) 0.05, (*c*) 0.10

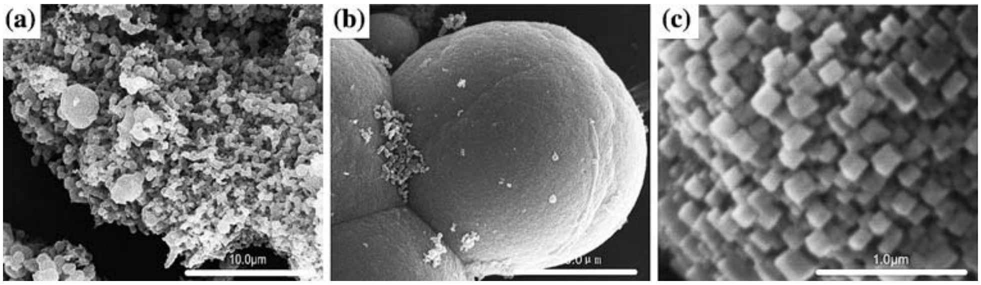

Fig. 7 SEM images of ZSM-5 obtained from SiO_2: $0.025Al_2O_3$:xTPABr:$40H_2O$ via sulfuric acid-catalyzed hydrolysis of TEOS with the crystallization time of 35 h at 180 °C. TPABr/SiO_2 ratios x are: **a** 0.00, **b** 0.05, **c** 0.10. The scale bars are: **a** and **b** 10 μm, **c** 1 μm

ratio gives the similar result to that of Fig. 7c. XRD patterns and SEM images for typical as-synthesized and as-calcined samples are compared in Figs. S1 and S2 (see Supporting Information). Obviously, there is no significant difference between the as-synthesized sample and as-calcined one in crystallinity and morphology.

Effect of H_2O/SiO_2 molar ratio

In the synthesis of zeolite, water provides an indispensable medium for the dissolution and diffusion of aluminosilicate [39]. Thus, the role of water content in the synthesis is a major factor to be considered. Herein, H_2O/SiO_2 molar ratio was adjusted from 5 to 80, and XRD results are shown in Fig. 8. It can be seen that the sample prepared at H_2O/SiO_2 ratio of five could not give any XRD peaks, and by increasing the H_2O/SiO_2 ratio to 10, ZSM-5 with low crystallinity was obtained. Highly crystallized ZSM-5 was achieved in the range 20–40 of H_2O/SiO_2 ratio, while the crystallinity increased gradually with the increase of the H_2O/SiO_2 ratio. However, when the water content in the synthesis gel further increased to 60 of H_2O/SiO_2, a lowered crystallinity of 80% was observed. At the very high H_2O/SiO_2 ratio of 80, only amorphous products appeared. It is thus concluded that the moderate H_2O/SiO_2 ratio of around 40 is optimal to produce zeolite ZSM-5 with pure phase and high crystallinity.

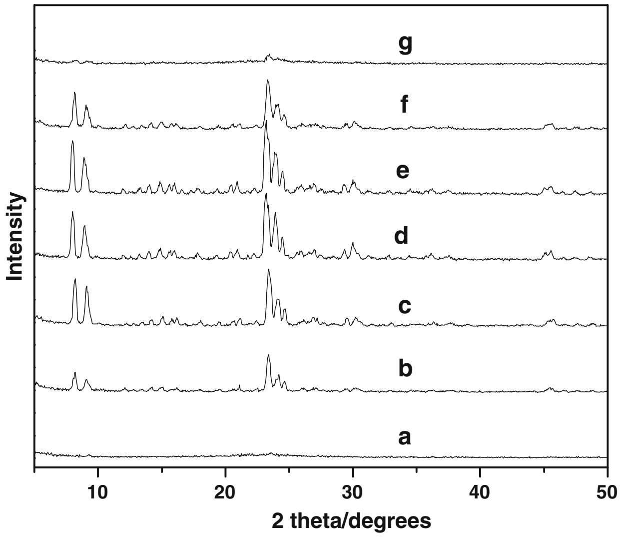

Fig. 8 XRD patterns of as-calcined samples prepared at H_2O/SiO_2 ratio of 5 (*a*), 10 (*b*), 20 (*c*), 30 (*d*), 40 (*e*), 60 (*f*), and 80 (*g*) via sulfuric acid-catalyzed hydrolyses of TEOS after 35 h of crystallization time at 180 °C with SiO_2/Al_2O_3 ratio of 40 and TPABr/SiO_2 ratio of 0.1

Actually, the ratio of H_2O/SiO_2 determines the concentration of the synthesis gel if the ratios of other substrates remain constant, and the viscosity of the synthesis gel changes with the altering of water content [40]. Therefore, it may influence the rates of nucleation and crystal growth. The observations from Fig. 8 are consistent with previous findings, i.e., for the low ratios of H_2O/SiO_2, the short distance between nutrients in the aqueous solution should have enhanced the nucleation and thus crystallization [41, 42], however, when the H_2O/SiO_2 ratio is too low (<20), the viscosity of the aluminosilicate gel would be too dense for substrates to diffuse freely and/or interact to each other, leading to the failed formation of ZSM-5 crystalline.

Influence of the crystallization pH value

Figure 9 shows the XRD patterns for samples obtained at various crystallization pH values. It is seen that not any crystalline phases were formed in the neutral reaction mixture. When the pH value increased from 8 to 10, a quick increase in crystallinity of the resulting ZSM-5 product was observed. It is obvious that the increase of alkalinity effectively induces the creation of the ZSM-5 crystalline from the amorphous aluminosilicate gel. However, at the higher pH value of 11, the degree of crystallinity of zeolite ZSM-5 decreased slightly, which is because the polycondensation of hydroxoaluminate and silicate ions is restricted by excess alkalinity [40].

Conclusions

In this study, we report in detail a novel method to facile synthesize small-sized ZSM-5 crystals by simply switching from conventional base-catalyzed hydrolysis of TEOS to the present acid-catalyzed system. The thus prepared ZSM-5 zeolite presents the crystal size of about 200 nm, which

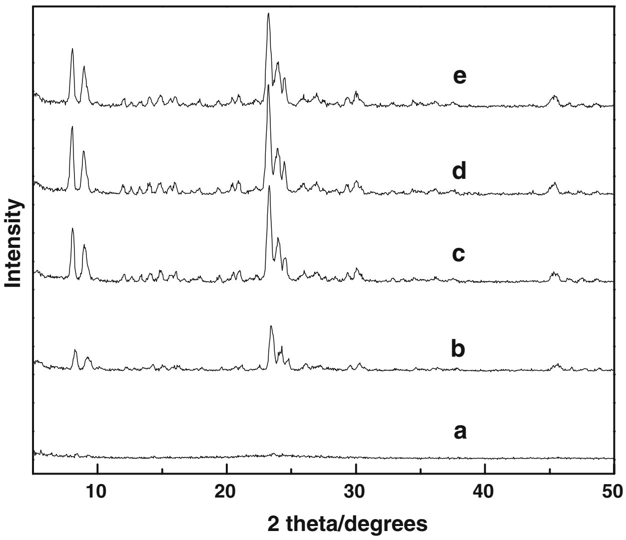

Fig. 9 XRD patterns for as-calcined samples synthesized at different crystallization pH values via sulfuric acid-catalyzed hydrolyses of TEOS after 35 h of crystallization time at 180 °C with the gel composition SiO_2:0.025Al_2O_3:0.1TPABr:40H_2O. (*a*) pH = 7, (*b*) pH = 8, (*c*) pH = 9, (*d*) pH = 10, (*e*) pH = 11

assembles into micro-sized single-crystal-like aggregate particles with a size around 10 μm. This morphology may endow the material with potential applications in catalysis and separation. Hydrothermal reaction temperature, pH value, TPABr/SiO_2 ratio, and H_2O/SiO_2 ratio for the synthesis gel mixture largely influence the crystallization process and the morphology of crystal ZSM-5. However, by this way, it is revealed that zeolite ZSM-5 can be successfully achieved in a broad window of synthesis conditions. Typically, with the sulfuric acid catalyzed hydrolysis of TEOS, the pure ZSM-5 with the crystallinity of 100% is obtained within 35 h of crystallization time at 180 °C of crystallization temperature with TPABr/SiO_2 molar ratio of 0.1 and H_2O/SiO_2 molar ratio of 40 in the synthesis gel mixture of pH 10.

Acknowledgements This study is supported by the Key Natural Science Foundation for Universities of Jiangsu Province (06KJA53012), National Natural Science Foundation of China (No. 20776069) and Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT 0732).

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