



Additive-free synthesis of mesoporous FAU-type zeolite with intergrown structure

Xiaoli Jia¹, Lu Han¹, Yanhang Ma² and Shunai Che^{1*}

ABSTRACT Hierarchical porous zeolites attract great attention because of their porosity on different scales to improve molecular diffusion. Here, we report mesoporous Faujasite (FAU) zeolite nanosheets with intergrown structure synthesized in an additive-free system. The sample was composed of uniform nanosheets with a slice thickness of ~50 nm, which held a honeycomb-like structure with abundant mesopores. This material exhibits both microporous and mesoporous structure: the intrinsic micropores with a diameter about 0.74 nm in the zeolite framework and the mesopores with a diameter about 10 nm existing within the zeolite nanosheets. The Si/Al ratios can be adjusted from 1.1 to 1.9 (zeolites X or Y). In addition, this simple and environment-friendly method may provide inspiration to the synthesis of other hierarchical zeolites.

Keywords: mesoporous zeolite, additive-free synthesis, intergrown structure

INTRODUCTION

Zeolites, crystalline microporous materials with pores and channels in molecular scale, are of great importance for industrial application [1–4]. However, the single micropore usually limits the molecule diffusion and fails to catalyze organic molecules in large dimensions. This problem can be solved by shortening effective diffusion path lengths [5–7], which has been achieved by miniaturizing zeolite crystals, delaminating or exfoliating layered zeolites, and introducing mesopores into zeolite particles [8]. Among these solutions, hierarchical zeolites combine intrinsic micropores and bypass-interconnected mesopores and therefore, enhance the micropore accessibility and molecular traffic within zeolite particles.

Hierarchical zeolites show an enhanced accessibility of the active framework for the reactants with different

molecular dimensions compared to conventional zeolites. Therefore, a lot of strategies including top-down desilication by alkali treatment [9–11], and bottom-up directed by hard [12–17] and soft template [18–34] have been proposed to synthesize meso-micro or macro-meso-micro zeolites. However, desilication is not suitable for the zeolite at low Si/Al molar ratio such as FAU, LTA, etc. Hard template method requires multistep procedures and is not favorable for large scale production. Alternatively, soft-template method is a simple and universal strategy to synthesize mesoporous zeolites.

FAU-type zeolite, a highly hydrophilic large-pore zeolite with a pore diameter of 0.74 nm at a low Si/Al molar ratio, is widely used in separation process (zeolite X) and catalytic conversion (zeolite Y). There are a few reports about the creation of additional porosity by soft template method [35–38], such as organosilane surfactants, ionic liquid and so on. For example, 3-(trimethoxysilyl)propyl hexadecyl dimethyl ammonium chloride (TPHAC) was used as surfactant to synthesize mesoporous FAU-type zeolite nanosheets with intergrown structure. The hierarchically branched FAU with house-of-cards like morphology contains three pore systems: the micropores in FAU framework, mesopores in the nanosheets and macropores interstices between the nanosheet stacks. However, this method holds another drawback that organic-template is not environmentally friendly, and they are non-recyclable and expensive. Furthermore, hierarchical FAU zeolites synthesized by soft-template method usually holds low Si/Al ratio (<1.5), which caused relative low thermal stability. Therefore, the synthesis of hierarchical FAU zeolite with high thermal stability through a cheap way is particular important for industrial application.

Herein, we report an approach to synthesize hier-

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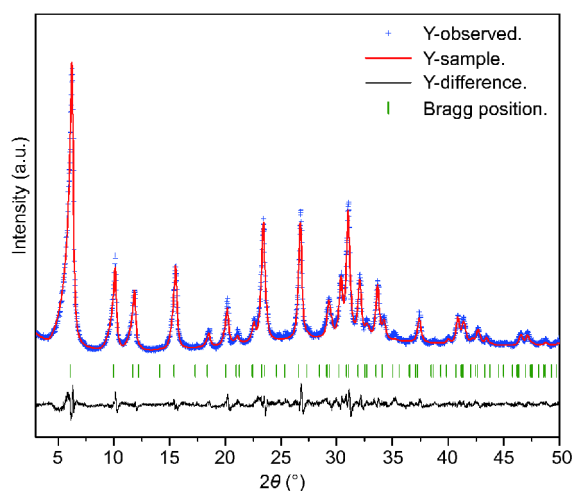


Figure 1 XRD patterns of the as-made mesoporous FAU zeolite crystallized at 60°C for 24 h. Vertical ticks correspond to line indexing of the FAU phase. Difference plots between calculated and experimental points are shown at the bottom. The synthesis molar composition was 1 SiO₂: 0.2 Al₂O₃: 4.5 Na₂O: 180 H₂O.

archical FAU zeolite by sequential intergrowth without any organic or inorganic additions. The selection of optimized synthesis conditions that can form interlaced nanosheets seems to be a key to achieving hierarchical structure. We particularly focus on the FAU zeolite because it is widely used in industrial process due to its 12-ring in the framework and high thermal stability. To our knowledge, the synthesis of FAU zeolites with hierarchical structure and adjustable Si/Al ratio under no template has not been reported before. We hope our environmentally and low-cost approach to create mesopores in zeolite can provide help for industrial production.

EXPERIMENTAL SECTION

Synthesis of zeolite materials

In a typical synthesis of FAU zeolites, 7 g sodium hydroxide (AR, solid) was first dissolved in water and then the solution was divided into two parts. 7.1 g Na₂SiO₃·9H₂O (AR, solid) was added to one part and 0.82 g sodium aluminate (96%, solid) was added to another, the two solutions were mixed and stirred for 5 h in an ice bath. Then the mixture with the composition of 1 SiO₂: 0.2 Al₂O₃: 4.5 Na₂O: 180 H₂O was transferred into Teflon autoclaves in a static environment at 60°C. After a crystallization period, the final products were filtered, washed with distilled water and dried at 60°C overnight.

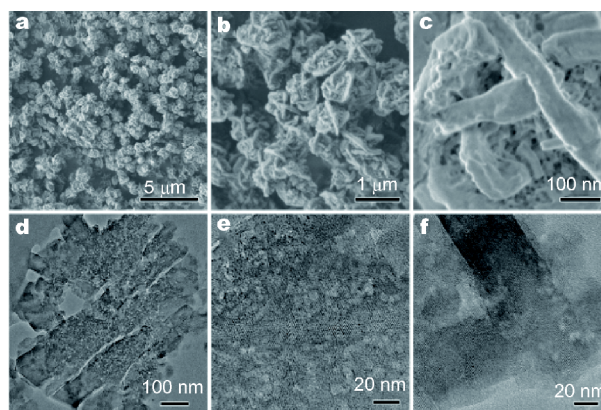


Figure 2 SEM (a–c) and TEM images (d–f) taken at different magnifications of the sample shown in Fig. 1.

Characterizations

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer D/max-III A equipped with Cu K α radiation (40 kV, 30 mA). SEM was conducted on a JEOL JSM-7401F electron microscope operated at 1 kV and JEOL JSM-7800F electron microscope operated at 0.3 kV. HRTEM was performed using JEOL JEM-2100 microscope operating at 200 kV (Cs = 1.4 mm, point resolution of 2.3 Å). The nitrogen adsorption/desorption isotherms were measured at 77 K using an ASAP 2010 M+C analyzer after the samples were degassing at 150°C for 12 h. For element analysis, the samples were first dissolved in hydrofluoric acid (50% in water) and nitrohydrochloric acid solution, then steaming on the electric heating plate. Finally, the dried sample was extracted by dilute nitrohydrochloric acid. The element analysis of Si, Al and Na was determined from the inductively coupled plasma analysis (ICP, Perkin-Elmer 3300DV) and Elementar Vario-ELIII IRMS analyzer.

RESULTS AND DISCUSSION

The hierarchical FAU zeolite was crystallized at 60°C for 24 h without any additives. The wide-angle X-ray diffraction (XRD) patterns of the samples shown in Fig. 1 verify that high-quality FAU zeolite was obtained, as the competing crystalline phases such as zeolite LTA and zeolite P were not observed. The phase purity was also identified by corresponding SEM images (Fig. 2a–c). The Si/Al molar ratio was 1.1, which is in the range of 1.0–1.5 for FAU-type zeolite X.

The representative SEM images (Fig. 2a–c) of hierarchical FAU zeolites show that the sample exhibits a uniform flower-like morphology with an average size of about 1 μ m. The flower-like particles are composed of

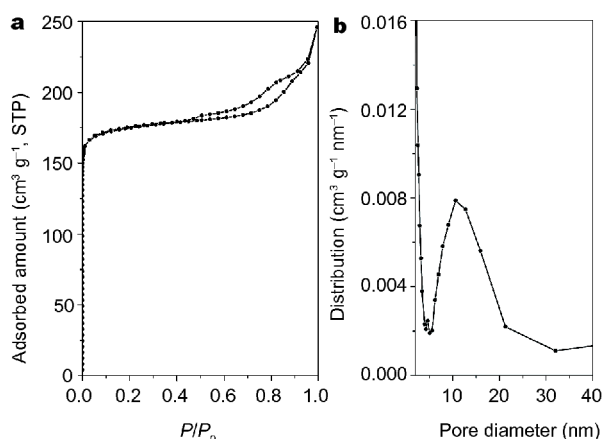


Figure 3 Nitrogen physisorption isotherms (a) and pore size distribution (b) of mesoporous FAU zeolites shown in Fig. 1.

nanosheets with a slice thickness of ~ 50 nm with a honey-like structure, which was further confirmed by the TEM images (Fig. 2e, f). The intergrowth between two nanosheets is clearly shown in Fig. 2c. Fig. 2e, f show TEM images of sliced thin section of the as-prepared sample. The low-magnification TEM image (Fig. 2d) shows the inner layer was constituted by honeycomb structure and the outer layer was single crystal. HRTEM image (Fig. 2e) shows abundant mesopores with an average diameter of ~ 10 nm in the nanosheets.

The microporous and mesoporous structure of hierarchical FAU zeolites was measured by nitrogen sorption analysis (Fig. 3). The adsorption-desorption isotherms that exhibit a steep increase below $P/P_0=0.02$ is the characteristic of microporous materials. As expected, a hysteresis loop at the relative pressure P/P_0 of 0.4–0.8 indicates the presence of mesopores. The zeolitic nanosheets characteristic of microporous materials. As expected, a hysteresis loop at the relative pressure P/P_0 of 0.4–0.8 indicates the presence of mesopores. The zeolitic nanosheets exhibits mesopores in a diameter of around 10 nm according to the pore size distribution curve, which is in accordance with TEM. A high Brunauer–Emmett–Teller (BET) surface area of $544 \text{ m}^2 \text{ g}^{-1}$ and Langmuir surface area of $850 \text{ m}^2 \text{ g}^{-1}$ and a total pore volume of $0.39 \text{ cm}^3 \text{ g}^{-1}$ were calculated with the meso- and micropore volume being $0.13 \text{ cm}^3 \text{ g}^{-1}$ and $0.26 \text{ cm}^3 \text{ g}^{-1}$, respectively.

The synthesis condition and the composition greatly affect the structure of the zeolite. The key factor in the synthesis of mesoporous FAU zeolite in this additive-free system is the precise control of the aging temperature, Si/Al and OH⁻/Si. We carefully investigated the compo-

sition change, while keeping other factors constant to achieve the full synthesis conditions.

The XRD patterns and the SEM images (Fig. S1) show that amorphous aluminosilicate was obtained at the low aging temperature of 40°C , as the low intensity of the XRD pattern and the amorphous phase in the SEM image. Very weak peaks of FAU appear when the aging temperature was 50°C , indicating the lower crystallinity. Relatively high crystalline FAU zeolite was obtained when the aging temperature was 60°C and the sample holds a flower-like morphology. When the temperature was increased to higher than 60°C , bulk FAU zeolites were synthesized (Fig. S1e, f). The formation of a zeolite with poor crystallinity at low temperature and bulk structure at high temperature are both unfavorable for the catalytic reaction including bulk molecules. Therefore, the temperature of 60°C was considered to be the most appropriate to direct the mesoporous FAU zeolites.

In order to study the effect of the Si/Al molar ratios on the formation of mesoporous FAU zeolite, the synthesis was carried out with different molar ratios of Si/Al at 60°C for 24 h. As FAU-type zeolite is a kind of aluminum-rich microporous zeolite, we adjusted the Si/Al ratio from 1 to 4 (Figs S2, S3). The XRD patterns clearly show that low Si/Al ratio results in the impure phase of LTA, the typical cubic morphology can be observed from the SEM images (Fig. S3a, b). Although ratios of Si/Al above 3 can produce pure FAU zeolite, all the samples show bulk morphology (Fig. S3e, f). From our results, the mesoporous FAU zeolite can only be synthesized under the synthetic gels with ratios of Si/Al between 2 to 3. Furthermore, we investigated the influence factor of the OH⁻/Si molar ratios (Figs S4, S5). Low OH⁻/Si molar resulted in amorphous phase, while high OH⁻/Si molar resulted impure phase. The OH⁻/Si molar between 7 to 9 could direct FAU zeolite without any other phase, the morphology changed from bulk to flower-like structure.

To investigate the formation process of mesoporous FAU zeolite in this template-free system, several samples were collected during the synthesis procedure. Fig. 4 shows the XRD patterns of the representative samples at different crystallization times. The sample collected at 6 h exhibits a broad peak that suggests an amorphous structure. The sample was partially crystallized when aging time increased to 12 h as the representative diffraction peaks appeared. The stronger diffraction peaks of FAU zeolite at 24 h indicated that high quality of FAU zeolite was obtained. As the crystallization time increases, the crystal structure remains unchanged, suggesting the relative high thermal stability.

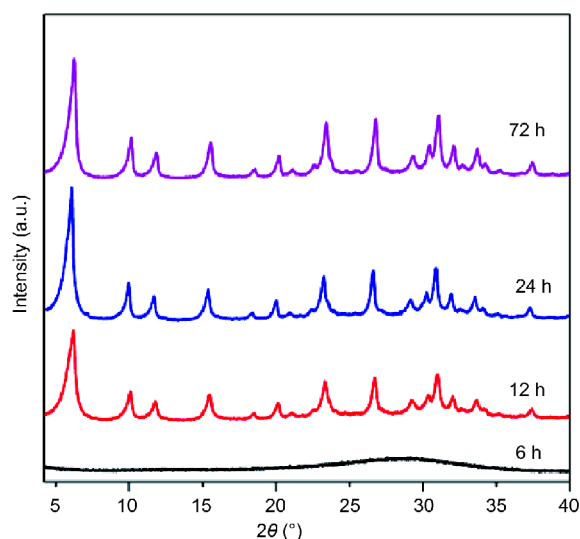


Figure 4 XRD patterns of the as-made mesoporous FAU zeolite for various aging times at 60°C. The synthesis molar composition was 4.5 Na₂O: 0.2 Al₂O₃: 1 SiO₂: 180 H₂O.

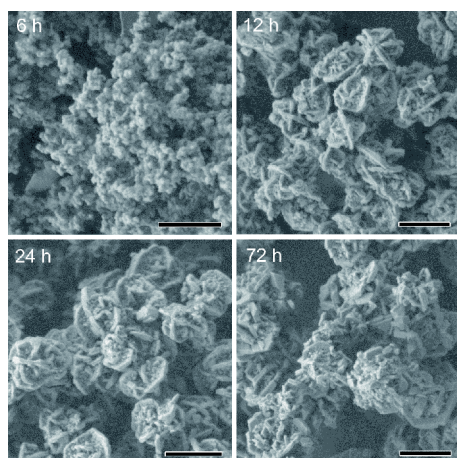


Figure 5 SEM images of the as-made hierarchical FAU zeolite. The scale bar in the SEM images was 1 μm.

The SEM image (Fig. 5) show the amorphous structure possesses a spherical-like morphology. The flower-like morphology was formed with the prolonging of the crystallization time to 12 h and the morphology remained unchanged when the crystalline time was extended to 24 h. All the samples show hierarchical structure according to the nitrogen physisorption isotherms and pore size distribution (Fig. 6). However, the mesopore surface area and volume decrease when the aging time is 72 h while the micropore textures remain the same (Table S1) because of the Ostwald ripening.

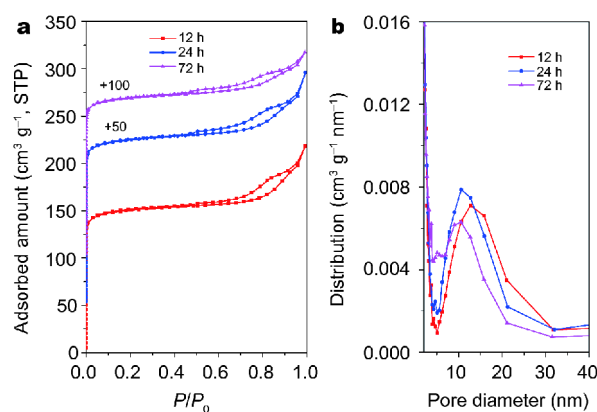


Figure 6 Nitrogen physisorption isotherms (a) and pore size distribution (b) of mesoporous FAU zeolites.

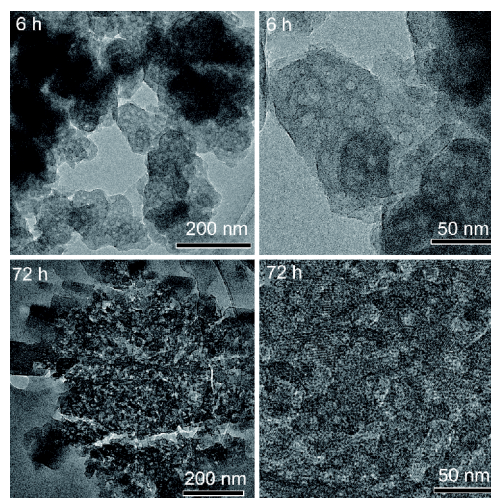


Figure 7 TEM images of the as-made mesoporous FAU zeolite.

The TEM images of the sample collected at 6 h and 72 h were taken (Fig. 7), it is obvious that the amorphous sphere exhibits hollow structure. We speculated the mechanism of the formation of mesoporous FAU zeolites according to the crystal growth process. The both existence of crystallization and desolution-recrystallization due to the high alkalinity in the synthesis system would cause the central hole. The initial amorphous aluminosilicate would be gradually turned into crystalline phase while the mesoporous structure remained with the extension of aging time. Furthermore, the relatively lower crystalline temperature weakened the effect of Ostwald ripening, which avoids the formation of bulky structure. However, the condensation of the silicon oxygen bond caused dense skeletal density which led to the shrinkage of mesopores during the crystallization process. There-

fore, the final mesoporous FAU zeolite with intergrown structure was formed. Furthermore, Si/Al molar ratio could be adjusted from 1.1 to 1.9 (Table S2) by changing the composition of the reactants.

CONCLUSIONS

Mesoporous FAU zeolites with intergrown structure were successfully synthesized under a mild condition without any organic or inorganic additives. Compared to the FAU nanosheets templated by TPHAC or other organic templates, the sample obtained by this method has a high Si/Al molar ratio, meaning higher thermal stability. Additionally, the additive-free system is low-cost and experimentally friendly, which possess great potential application value in industry. We hope our approach will provide more options and insight into the prospective synthesis of hierarchically zeolites with different framework type.

Received 14 November 2017; accepted 03 February 2018;
published online 10 February 2018

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Acknowledgements This work was supported by the National Natural Science Foundation of China (21533002 and 21571128) and the National Excellent Doctoral Dissertation of China (201454).

Author contributions Che S designed the experiment and led the project. Jia X synthesized the mesoporous FAU zeolites and performed the SEM, XRD, N₂ adsorption-desorption measurements. Jia X wrote the paper with support from Che S, Lu H and Ma Y. All authors contributed to the general discussions.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.



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无添加剂体系合成具有共生结构的介孔FAU沸石

贾晓利¹, 韩璐¹, 马廷航², 车顺爱^{1*}

摘要 本文用无添加剂体系合成了具有共生结构的介孔FAU沸石. 该材料具有由约50纳米厚度的纳米片堆积形成的花状形貌, 而且具有两种孔道体系: 沸石骨架本身的微孔和存在于纳米片内部的晶间介孔. 通过对合成条件精确的控制以及对反应物比例的筛选, 分别合成了介孔X型(硅铝比<1.5)和Y型(硅铝比>1.5)沸石. 温和的温度以及高碱度使得在成核初期发生结晶-溶解-重结晶过程是形成介孔FAU沸石的关键条件. 该合成体系用简单和低成本的方法在FAU沸石中引入介孔, 有望突破沸石在大分子催化中的限制, 将有可能应用于工业化生产.