Effects of crystallization time and composition of gel for preparing of zeolite K-F

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Zeolite K-F crystals were prepared by a hydrothermal route, the effects of crystallization time as well as composition of gel (K_2O/SiO_2 and Al_2O_3/SiO_2) on the final samples were studied. The results displayed that when heating time was increased to 24 h, cubic aggregates with well-developed faces were observed. In detail, the parent zeolite aggregates with size variation (2-5 um) were composed of flattened cuboid shaped primary crystals. Higher K_2O/SiO_2 ratio was favorable for the generation of smaller individual primary zeolite K-F nanosized crystals, resulting in forming large steady congregated agglomerates. However, too strong alkalinity resulted in amorphous materials produced. Moreover, batch molar ratio Al_2O_3/SiO_2 =0.15 was a single phase of zeolite W; Well-crystallized zeolite K-F samples were obtained at Al_2O_3/SiO_2 ratios of 0.65, 0.92, 1.45, 2.03 and 2.34. With the Al_2O_3/SiO_2 was increased to 3.05, needle-type hexagonal cancrinite crystals were generated.

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1. Introduction

Zeolites are porous aluminosilicates with tetrahedral structural units [1,2]. The unique frameworks in zeolites, endow them with high surface area, special pore structure, strong acidity as well as superior hydrothermal/thermal stability [3-5]. Zeolites have been applied widely in petrochemical and fine chemical industries [6-9].

Most applications of zeolites would be dependent on the frameworks. Nevertheless, morphology of samples also plays a key role in zeolitic application. In recent years, numerous attempts had been absorbed in investigation of the factors which dominated particle properties and crystallization way of the final samples. These studies demonstrated that heating condition as well as composition of gel were major factors that controlled zeolitic properties [10-12]. Zhang et al [13]. had reported the preparation of sodalite by hydrothermal processes, it revealed that the obtained products were pure phases of zeolite NaA, sodalite, and cancrinite with extending heating. Moreovre, well-crystallized cancrinite crystals was seen with increased H₂O/SiO₂ ratio, whereas higher water content in gel led to analcime produced. Nazir et al [14]. pointed that higher Na₂O/Al₂O₃ ratio would reduce the nucleation periods, which caused the product became smaller with less regular in shape; while at Na₂O/Al₂O₃=17, unexpected zeolite NaP was formed. Gao et al [15]. pointed that lower content of water facilitated rod-like SUZ-4 crystal generation, while higher water content favored fiber-like SUZ-4 particle production. In addition, Kulprathipanja et al [16]. found that when SiO₂/Al₂O₃>10, ZSM-5, zeolite NaY and beta were synthesized; $SiO_2/Al_2O_3 \le 5$, the samples obtained were low silica zeolites. From above results, although zeolite samples were thermodynamically unstable stages, kinetics crystallizations were also key parameters to be considered. Here, zeolite K-F crystals were prepared by a hydrothermal route. The effects of heating time as well as composition of gel (K_2O/SiO_2 and Al_2O_3/SiO_2) on the final samples and particle properties (crystal size, crystal shape) were studied.

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2. Experimental

2.1. Preparation

Zeolite K-F was prepared by a hydrothermal way. Firstly, a aluminate solution was obtained by mixing potassium hydroxide (99.99%, Merck) as well as aluminum hydroxide (98%, Merck) in demineralized water. Thereafter, Ludox ZS-30 (30wt% SiO₂, Zhejiang Yuda Chemical Co. Ltd.) was dropped into aluminate solution under stirring, the compositions of precursor hydrogel were x K₂O: 1.0 SiO₂: y Al₂O₃: 54.63 H₂O on a molar basis, where x=0.08-7.85, and y=0.15-3.05. The resulting mixture was agitated for 30 min, hydrothermally treated at 120 °C in sealed polypropylene bottles. Finally, the synthesized samples were washed thoroughly with demineralized water, and dried overnight at 90 °C.

2.2. Characterization and analyses

X-ray data (XRD) were made on a Philips PW 1830 diffractometer with Cu-K α radiation. Scanning electron microscopy (SEM) pictures were conducted using a LEO 1530 TFE microscope. Infrared transmission spectra (FTIR) were measured by a Bruker Tensor 27 spectrometer using KBr pellet method. N₂ adsorption-desorption isotherms were made at -196°C using a Quantachrome Nova 2000e analyzer. Particles size distribution curves of products were obtained by a Malvern Mastersizer 2000 laser particle size analyzer.

3. Results and discussion

3.1. Effect of crystallization times

The XRD patterns of samples prepared at the gel mole ratio 1.25 $K_2O:1.0$ SiO₂:0.82 Al₂O₃:54.63 H₂O for different heating times are displayed in Fig. 1. The products obtained is amorphous after 3 h of hydrothermal reaction (Fig. 1a). After 5 h, some very weak XRD diffraction peaks, corresponding to EDI-type structure are observed, confirming that the product contains plentiful amorphous materials (Fig. 1b). A rapid enhancement in crystallinity is seen between 5 and 24 h crystallization (Fig. 1b-e). A well-crystallized zeolite K-F sample is formed with crystallization time of 24 h (Fig. 1e). However, with extending reaction time up to 72 h, diffraction intensity of the zeolite sample would not intensify (Fig. 1f), suggesting that the crystallization of zeolite K-F has been completed within 24 h. Wong et al [17]. reported that EDI-type phase was unstable, which could transform into more thermodynamically stable zeolite LTJ as extending heating. However, in this study, no zeolite LTJ phase is detected after 72 h of hydrothermal crystallization.



Fig. 1. XRD patterns of synthesized samples with various heating times. (a) 3 h, (b) 5 h, (c) 7 h, (d) 16 h, (e) 24 h, and (f) 72 h.

Fig. 2 displays FT-IR curves of corresponding samples. As seen, the 3 h crystallization sample would not exhibit characteristic zeolite K-F adsorption bands, meaning the prepared product is amorphous aluminosilicat (Fig. 2a). The intensity of absorption band around 856 cm⁻¹, assigned to T-OH (T= Al or Si) weakens with extended heating time, suggesting the quantity of amorphous phase in the product would gradually decrease (Fig. 2b-d). This may be attributed to T-OH bonds are transformed into T-O-T bonds through phase rearrangement in hydrogel matrix [18]. After 24 and 72 h crystallization, this band for T-OH completely disappears, and five absorption bands (432, 528, 569, 607 and 665 cm⁻¹) could be clearly seen (Fig. 2e-f). Also, many researchers owed the bands to pure phase zeolite K-F units [17,19,20]. The results are consistent with XRD data.



Fig. 2. IR spectra of synthesized products with various heating times. (a) 3 h, (b) 5 h, (c) 7 h, (d) 16 h, (e) 24 h, and (f) 72 h.

Fig. 3 displays the SEM pictures of products. From Fig. 3a, the obtained samples consisting of aggregated gel particles. It had been reported that the zeolitic nuclei were wrapped by amorphous masses, which was confirmed on synchrotron by situ XRD [21]. Cubic particles corresponding to zeolite K-F accompany with amorphous materials are observed after 5, 7 and 16 h crystallization (Fig. 3b-d). Notably, the 5 h crystallized samples exhibit a similar morphology to that of 7 and 16 h crystallized products, but with smaller particle sizes. Obviously, the 5 h products are incompletely crystalline according to XRD data, the crystals could continue to grow, reflected in the SEM pictures with less amorphous materials are observed as the extension of crystallization time [22]. After 7 h, the morphology of the crystalline zeolite samples becomes more stable. When the reaction time extends to 24 and 72 h, cubic aggregates are obtained (Fig. 3e-f). Additionally, the parent zeolite aggregates with size variation (2-5 um) are composed of flattened cuboid shaped primary crystals.





Fig. 3. SEM results for prepared samples with various heating times. (a) 3 h, (b) 5 h, (c) 7 h, (d) 16 h, (e) 24 h, and (f) 72 h.

3.2. Effect of K₂O/SiO₂ ratios

Fig. 4 displays the XRD patterns of products prepared from x K_2O : 1.0 SiO₂: 0.82 Al₂O₃: 54.63 H₂O after 24 h crystallization. Obviously, the product synthesized with $K_2O/SiO_2=0.08$ is ascribed to zeolite A (Fig. 4a). At $K_2O/SiO_2=0.21$, zeolite A and traces of sodalite phase are observed in the end sample (Fig. 4b). Upon increasing K_2O/SiO_2 ratio to 0.65, a mixture of both crystalline zeolite A and zeolite K-F are obtained (Fig. 4c). Well-crystallized pure phase zeolite K-F products are generated at relatively higher K_2O/SiO_2 molar ratios of 1.05, 1.25, 3.42 and 4.45, respectively (Fig. 4d-g). Therefore, the above results confirm that mild alkalinity is profit to form zeolite K-F. As reported in the literature [23], the nucleation rate would improve with the increase of supersaturation in gel mixture. Nevertheless, excessive alkalinity promotes the autolysis of zeolite produced incipiently, then causes the decline in crystallinity of final product [24]. In case of $K_2O/SiO_2=7.85$, only amorphous material is obtained (Fig. 4h).



Fig. 4. XRD patterns of synthesized products with various K₂O/SiO₂ ratios. x: (a) 0.08, (b) 0.21, (c) 0.65, (d) 1.05, (e) 1.25, (f) 3.42, (g) 4.45, and (h) 7.85.

The SEM pictures of samples obtained with K_2O/SiO_2 ratios of 0.21, 0.65, 1.05, 1.25, 3.42, and 4.45 are displayed in Fig. 5. From Fig. 5, wool ball-like shaped sodalite crystals and some cubic particles due to zeolite A are observed at $K_2O/SiO_2=0.21$ (Fig. 5a). While at $K_2O/SiO_2=0.65$, the co-existence of zeolite A with cubic aggregates corresponding to zeolite K-F are obtained (Fig. 5b). Also, it is noted that zeolite A products obtained at high K_2O/SiO_2 molar ratio exhibits bigger crystal size. With the K_2O/SiO_2 molar ratio is increased to 1.05, 1.25, 3.42 and 4.45, larger cubic secondary particles of zeolite K-F are observed (Fig. 5c-f).

Particle size distribution curves corresponding to zeolite K-F products are exhibited in Fig. 6. The zeolite K-F samples obtained with K_2O/SiO_2 molar ratios of 1.05, 1.25, 3.42 and 4.45 have the average particle sizes of 4.1, 4.6, 8.0 and 8.9 um, and the particle size distribution ranges of 2.74–5.55, 2.82–6.20, 6.13–9.95 and 6.24–11.08 um, respectively. And in detail, the zeolite K-F particles synthesized at higher alkalinity are composed of many smaller primary nanocrystals. As the increase of alkalinity would improve structure-forming alkali metal ion concentration which induces the nuclei generation. Therefore, a decrease in primary crystal size with increased alkalinity resulted from increasing quantity of nuclei generated in gel reactant. The smaller flattened cuboid primary crystals form bigger cubic parent zeolite particles by agglomerating, which are favourable to zeolitic stabilization [25,26].

The N₂ adsorption–desorption isotherms for zeolite K-F samples obtained with K₂O/SiO₂ ratios of 1.05, 1.25, 3.42 and 4.45 are displayed in Fig. 7. All the products present a typical type IV with type H₃ hysteresis loop, such phenomenon is ascribed to the larger N₂ probe molecule size than EDI zeolite pore diameter [19]. Also, it is noted that the samples obtained at higher K₂O/SiO₂ ratios show better sorption capacity, and this arises from smaller primary crystals as well as lower packing densities. As a consequence, this zeolite could be used in helium (σ =2.60 Å) as well as hydrogen (σ =2.89 Å) separation, hydrogen storage and film deposition for sensing application.



*Fig. 5. SEM results for prepared samples with various K*₂*O*/*SiO*₂ *ratios. x: (a) 0.21, (b) 0.65, (c) 1.05, (d) 1.25, (e) 3.42, and (f) 4.45.*



Fig. 6. Particle size distribution curves of prepared samples.



Fig. 7. N_2 adsorption-desorption isotherms for samples obtained with various K_2O/SiO_2 ratios. x: (a) 1.05, (b) 1.25, (c) 3.42, and (d) 4.45.

3.3. Effect of Al₂O₃/SiO₂ ratios

Fig. 8 displays the XRD patterns of products synthesized from 1.25 K₂O: 1.0 SiO₂: y Al₂O₃: 54.63 H₂O for 24 h reaction. As seen, the obtained samples is a single-phase zeolite W at Al₂O₃/SiO₂=0.15 (Fig. 8a). At Al₂O₃/SiO₂=0.41, both of crystalline zeolite W and zeolite K-F is observed (Fig. 8b). When the Al₂O₃/SiO₂ ratio is increased to 0.65, 0.92, 1.45, 2.03 and 2.34, well-crystallized pure zeolite K-F samples are obtained, respectively (Fig. 8c-g). It is because that correspondingly higher concentration of Al³⁺ favors small silicate species 8-membered rings formation with increased aluminum hydroxide in gel mixture [27,28]. However, with Al₂O₃/SiO₂=3.05, zeolite K-F accompany with cancrinite phase are observed in the end product (Fig. 8h).



Fig. 8. XRD patterns of prepared samples with various Al₂O₃/SiO₂ ratios. y: (a) 0.15, (b) 0.41, (c) 0.65, (d) 0.92, (e) 1.45, (f) 2.03, (g) 2.34, and (h) 3.05.

Zeolite W а Zeolite K-Zeolite W d e Cancrinite h C Zeolite K-F

*Fig. 9. SEM pictures of synthesized products with different different Al*₂O₃/SiO₂ *ratios. y: (a) 0.15, (b) 0.41, (c) 0.65, (d) 0.92, (e) 1.45, (f) 2.03, (g) 2.34, and (h) 3.05.*

Fig. 9 displays the SEM pictures of samples. As seen, the products generated at Al₂O₃/SiO₂=0.15 exhibit only bouquet-like shaped crystals due to zeolite W (Fig. 9a). Spherical shaped morphology of zeolite K-F crystals and some bouquet-like particles are obtained with $Al_2O_3/SiO_2=0.41$ (Fig. 9b). While at $Al_2O_3/SiO_2=0.65$, the bouquet-like shaped crystals disappear and only spherical particles of zeolite K-F are observed. And in detail, the samples are composed of aggregated particles (Fig. 9c). When the Al_2O_3/SiO_2 ratio is increased to 0.92 and 1.45, only cubic agglomerates consisting of flattened cuboid shaped primary zeolite K-F crystals are achieved (Fig. 9d-e). Whilst, the zeolite K-F obtained from Al₂O₃/SiO₂=2.03 give more nonuniform morphologies with both spherical and cubic shapes as shown in Fig. 9f. The cubic aggregates disappear and only spherical shaped particles are observed at Al₂O₃/SiO₂=2.34 (Fig. 9g). Additional, spherical secondary particles (2-5 um in diameter) are composed of primary nanocrystals with size in the range of 50-80 nm. Notably, zeolite K-F samples obtained with Al₂O₃/SiO₂ ratios of 0.65, 0.92, 1.45, 2.03 and 2.34 display similar particle sizes with different morphology, although higher Al₂O₃/SiO₂ ratio is beneficial to forming smaller primary zeolite K-F nanocrystals. These differences could be attributed to different Al contents cause different number as well as distribution of pre-nuclei in reaction mixture [29,30]. However, at Al₂O₃/SiO₂=3.05, spherical secondary particles accompany with some needle-type hexagonal cancrinite crystals are observed (Fig. 9h).

4. Conclusions

Well-crystallized zeolite K-F samples were obtained at crystallization temperature of 120 °C for 24 h, and in detail, the parent zeolite aggregates (2-5 um in diameter) were composed of small primary crystals with a flattened cuboid shape. High K_2O/SiO_2 ratio was favorable for the generation of smaller individual primary zeolite K-F nanosized crystals, which caused bigger cubic parent particles. However, too strong alkalinity resulted in amorphous materials produced. Moreover, batch molar ratio Al_2O_3/SiO_2 was very sensitive for zeolitic synthesis. The product obtained at $Al_2O_3/SiO_2=0.15$ was a single-phase zeolite W; At $Al_2O_3/SiO_2=0.41$, zeolite W accompanied with zeolite K-F were observed; High purity and well-crystallized zeolite K-F samples were formed with the Al_2O_3/SiO_2 ratios of 0.65, 0.92, 1.45, 2.03 and 2.34. While the Al_2O_3/SiO_2 was increased to 3.05, needle-type hexagonal cancrinite crystals were observed.

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