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Ceramics International 39 (2013) 5997–6003

CERAMICS INTERNATIONAL

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Short communication

Phase and morphology control of LTA/FAU zeolites by adding trace amounts of inorganic ions

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Received 5 December 2012; received in revised form 2 January 2013; accepted 3 January 2013
Available online 11 January 2013

Abstract

Zeolites were hydrothermally synthesized by adding different amounts of NaCl, KCl, NaF, or KF into a standard LTA (Lind type A zeolite) synthesis system and the effects of Cl^-, F^-, and K^+ on the phase selection were identified by comparing the obtained zeolites. The addition of trace amounts of the salts could change the resulting zeolites, and the cations and anions of the salts showed synergetic or antergic effects. Cl^- strongly promoted the formation of FAU (Faujasite type zeolite), whereas F^- favored FAU in a very low concentration but inhibited it in higher concentrations. K^+ favored the synthesis of LTA and could cooperate with F^- when adding KF in the synthesis system but offset the effect of Cl^- when adding KCl. The addition of ions also influenced the morphology of zeolites significantly. This study provides a simple approach to control the phase composition and morphology of zeolites and calls attention to the significant effects of impurities on hydrothermal synthesis, especially when using natural materials or industrial waste as feedstock.

Keywords: A. Powders: chemical preparation; B. Electron microscopy; B. Impurities; B. X-ray methods

1. Introduction

Both LTA (Linde type A, zeolite A) and FAU (Faujasite, zeolite X and Y) are commercially important zeolites widely used as adsorbents, catalysts or ion-exchangers. Structurally, they all contain sodalite cages as building units. For LTA, sodalite cages are linked by double four-rings (D4Rs) forming α cages, while for FAU, sodalite cages are linked by double six- rings (D6Rs) forming large cavities called supercages [1]. These two kinds of zeolites are also synthesized under similar conditions and usually formed simultaneously [2–11]. To obtain pure LTA or FAU without impure phases, synthesis parameters, such as alkali concentration, Si/Al ratio, aging time, and synthesis temperature, should be strictly controlled. A small variation in these parameters may result in impure zeolites. In some applications, a specific mixture of LTA/FAU may exhibit the best performance. For example, as a water-softener agent there was a synergistic effect when using LTA/FAU mixtures and the rates of ion exchange were greatly enhanced when using these mixtures compared to using either zeolite alone in the same Ca^{2+}/Mg^{2+} solution [12]. Therefore, it is necessary to elucidate the key parameters to govern the phase selection and achieve the controlling synthesis of LTA/FAU.

Alkali cations are fundamental components in the hydrothermal synthesis of zeolites. Besides balancing the negative framework charge of zeolites, alkali cations usually act as a key factor determining which zeolite is obtained [13]. This is also true for LTA/FAU synthesis. For example [8], both zeolite LTA and FAU can be synthesized from Na_2O–Al_2O_3–SiO_2–H_2O systems using tetramethylammonium cation (TMA^+) as structure-directing agent (SDA) and in this system the concentration of Na^+ plays a critical role for the phase selection of LTA/FAU. Without Na^+, neither LTA nor FAU can be synthesized. However, with the increase of Na^+ concentration the product gradually changes from pure FAU to pure LTA via the formation of FAU/LTA composite with increasing LTA fraction. Similar results were also reported by other authors [9–11].

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http://dx.doi.org/10.1016/j.ceramint.2013.01.005

Another important alkali cations influencing the phase selection of LTA/FAU is K^+. It was found that in K^+/Na^+ system K^+ can suppress the competitive crystallization of LTA resulting in the synthesis of FAU, though neither LTA nor FAU can be obtained in pure K^+ system. For example, Iwama et al. [5] investigated the synthesis of low silica FAU in the system of $2SiO_2:Al_2O_3:28.6(Na_2O+K_2O):500H_2O$. They found that when $K/(Na+K)<0.1$, zeolite LTA appeared as a predominant product, while when $0.1<K/(Na+K)<0.3$, both zeolite LTA and FAU were observed. When $K/(Na+K)>0.3$, pure FAU without any impurity was obtained, and when $K/(Na+K)>0.4$, sodalite phase (SOD) was generated.

Alkali cations can be introduced into the synthesis systems by two methods. The usual one is in the form of hydroxides such as NaOH and KOH, but the amount of alkali cations added in the systems is limited because OH^- ions acting as mineralizing agent significantly influence the crystallization process. Another method is in the form of soluble salts, but the corresponding anions of the salts will inevitably be introduced into the systems. Although up to now seldom investigation has been carried out, the effects of anions on the synthesis of zeolites are unignorable. For example, Kumar et al. [14] found that the addition of oxyanions, such as ClO_4^-, PO_4^{3-}, NO_3^-, SO_4^{2-}, CO_3^{2-}, AsO_4^{3-}, ClO_3^-, BrO_3^-, and IO_3^-, significantly enhanced the crystallization process of variety of zeolite structures. Toktarev and Echevskii [15] investigated the influence of the nature of anion in the tetraethylammonium salt on the selection of the formation zeolite beta and found that F^- and the anions of polybasic acids facilitated the formation of zeolite, whereas ClO_4^-, Br^-, and I^- ions inhibited its formation. However, Bosnar et al. [16] analyzed the kinetics of nucleation, crystal growth and entire process of crystallization of zeolite A by addition of equimolar amounts of different sodium salts (sulfate, acetate, chloride, iodide and phosphate) to the reaction mixture and concluded that only sodium ions and not the associated anions influenced the rate of crystal growth of zeolite A.

In this paper we synthesized a serial of zeolites by adding a different amount of common inorganic salts NaCl, KCl, NaF, and KF into a standard LTA synthesis system and identified the influence of Cl^-, F^-, and K^+ on the phase selection of LTA/FAU by comparing the zeolite phase obtained. Surprisingly, the phase of zeolites could be changed by the addition of trace amounts of the salts.

2. Experimental section

2.1. Synthesis

The batch formula and procedure of zeolite synthesis was based on a standard method of LTA synthesis [17], but a certain amount of inorganic salt (NaCl, NaF, KF or KCl) was added in the initial gel to examine the effect of the additives on the phase selection and crystal morphology of zeolites. The initial gel was prepared by mixing appropriate amounts of sodium hydroxide, sodium silicate, sodium aluminate and deionized water, and then a certain amount of inorganic salts was added. The mixture was stirred for 20 min and transferred into a 100 mL Teflon-lined stainless steel autoclave. The hydrothermal crystallization was carried out in static condition at 100 °C for 4 h. The solid product was filtered, washed with deionized water to about pH 8, and dried at 120 °C overnight. All chemical reagents used were of analytical grade.

The final molar composition of the synthesis mixture was $3.165Na_2O:1.926SiO_2:Al_2O_3:128H_2O:nX$, where X was NaCl, KCl, NaF, or KF, and n was from 0.002 to 1. The as-synthesized products were donated as S–*X*–*n*, and the control sample synthesized without additives was donated as S–0–0.

2.2. Characterization

XRD data were collected on a Y-2000 automated X-ray diffractometer system (Dandong Aolong Radiative Instrument Co., Ltd., China) with Cu K α radiation. FTIR spectra were obtained on a WQF-510 Fourier-transform infrared spectrometer (Beijing Rayleigh Analytical Instrument Corp., China) using the KBr disc method. Scanning electron microscopy (SEM) images were taken with a JSM-7500F (Jeol, Japan).

3. Results and discussion

3.1. Effect of cations and anions on zeolite phases

As mentioned above, both cations and anions of inorganic salts may influence the synthesis of zeolites. To identify the respective contribution of each ion, we added a certain amount of NaCl, KCl, NaF and KF, respectively, to a standard system of LTA synthesis and compared the phase compositions of synthesized products through X-ray diffraction patterns (Fig. 1). As can be seen, the addition of even a very small amount of these salts surprisingly resulted in completely different zeolites.

Without the addition of the salts in the synthesis system, the synthesized product (S–0–0) was not the expected pure LTA but contained some FAU impurities, indicating the competition of FAU and LTA in this synthesis system, though this system is classically used to synthesize LTA zeolite. Surprisingly, when adding a very small amount of NaCl to the synthesis system, the pure FAU phase without any contaminant (S–NaCl–0.002) was obtained, indicating NaCl favored the synthesis of FAU zeolite in this system. Considering the amount of Na^+ from the added NaCl was ignorable comprising with the Na^+ existed in the initial mixture, we could conclude that Cl^- strongly promoted the formation of FAU zeolite. Increasing NaCl to $n=0.1$ and 1, the resulted products were almost pure FAU only containing trace LTA (S–NaCl–0.1 and S–NaCl–1). In addition, the amount of NaCl also influenced the crystallinity of obtained zeolites. The XRD peak intensity of sample S–NaCl–0.1 was considerably higher than that of S–NaCl–0.002 and S–NaCl–1, indicating that sample S–NaCl–0.1 had better crystallinity.

Although Cocks and Pope [18] have found that the rate of synthesis of zeolite X increased strongly with Cl^-

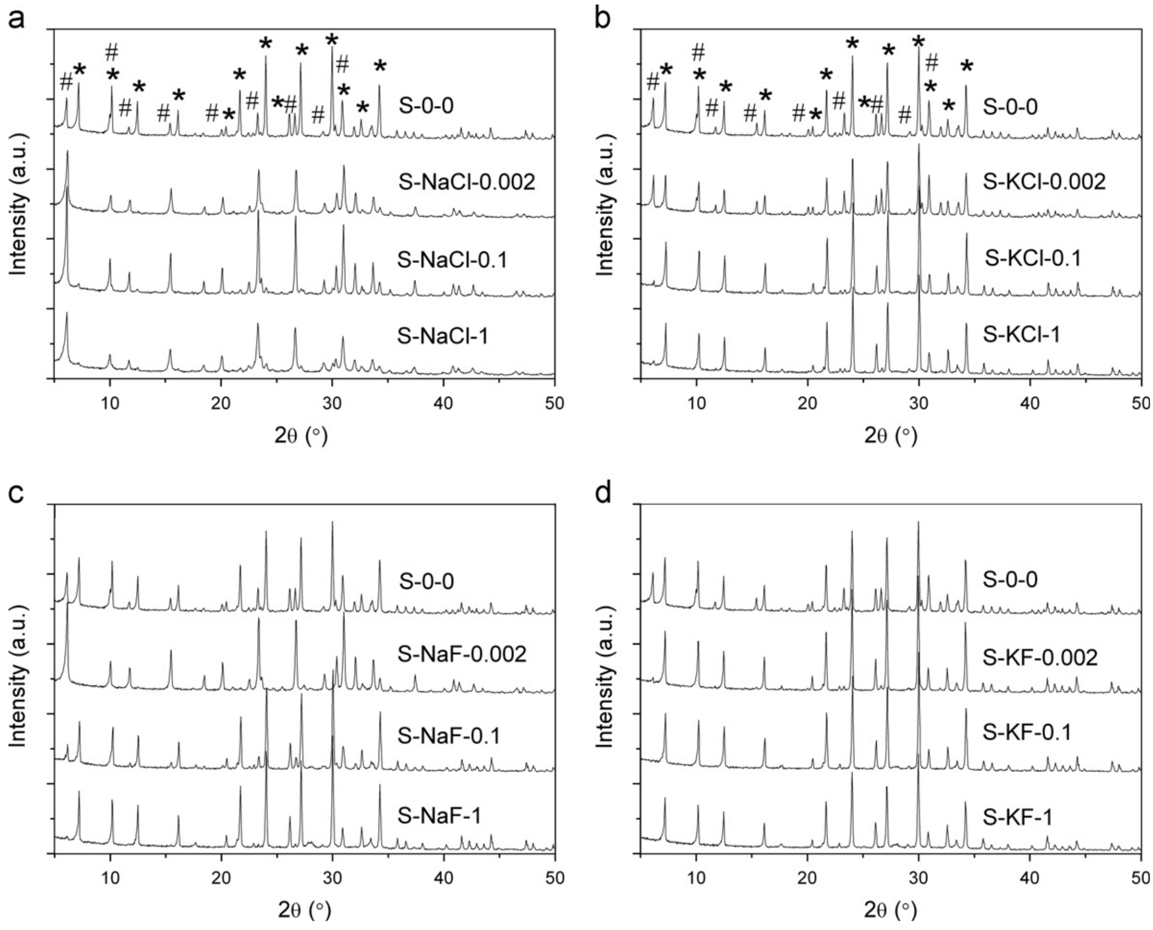

Fig. 1. XRD patterns of the as-synthesized samples by adding (a) NaCl, (b) KCl, (c) NaF, and (d) KF. * LTA, ♯ FAU.

concentration, the Cl^- concentration they used was considerably high. In addition, Zhu et al. [19] using NaCl as Na^+ source successfully synthesized not only pure FAU but also pure LTA single nanocrystals. They did not mention the effects of Cl^-, indicating Cl^- did not affect the formation of LTA in their system. However, our results showed that a trace amount of Cl^- could inhibit LTA and promote FAU formation in a LTA synthesis system.

When adding a trace amount of KCl to the initial mixture, the product obtained was a mixture of LTA/FAU (S–KCl–0.002). Increasing the amount of KCl the fraction of FAU in the zeolite mixture decreased (S–KCl–0.1). Under a higher amount of KCl, the product obtained was almost pure LTA only containing trace FAU (S–KCl–1). These results showed that K^+ offset the effect of Cl^- and favored the synthesis of LTA zeolite. It is worth to mention that in the literatures K^+ was considered to compress the formation of LTA and favor FAU synthesis [3–45]. However, our results indicated that K^+ could inhibit FAU and favor LTA synthesis.

To investigate the effect of F^- on the phase selection of LTA/FAU zeolites, a certain amount of NaF was added to the initial mixture. Surprisingly again, adding trace amount of NaF resulted in pure FAU zeolite without any impure phase (S–NaF–0.002), just like the result of adding a same amount of NaCl. However, with the increase of NaF, the LTA zeolite became dominant phase (S–NaF–0.1), and ultimately, almost pure LTA only containing trace FAU contaminant was obtained (S–NaF–1). These results indicated that F^- favored FAU in a very low concentration but inhibited it in higher concentrations.

F^- can instead of OH^- as mineralizers used in hydrothermal synthesis [20]. This method can be carried out at near neutral pH and this makes it easy to prepare high-silica zeolites, especially pure-silica zeolites that seem to be difficult to synthesize in the conventional OH^- media. To play the role of mineralizers the concentration of F^- in the initial mixture should be considerably high. The effects of F^- with very low concentration on the zeolite synthesis have not been reported.

Adding a trace amount of KF to the initial mixture resulted in almost pure LTA (S–KF–0.002), indicating K^+ was a strong LTA promoter, which offset the effect of F^-. With the increase of KF the products were completely pure LTA without any FAU contaminant (S–KF–0.1 and S–KF–1), indicating K^+ and F^- in the higher concentrations synergetically inhibited the FAU and favored the growth of LTA.

The effect of Na^+ added as NaCl or NaF did not emerged in above investigation due to Na^+ existed in a high concentration in the initial mixture.

3.2. *FTIR characterization of synthesized zeolites*

In addition to X-ray powder diffraction, infrared spectroscopy can also serve as a rapid and useful technique for characterizing the framework structure of zeolites, which can sometimes give more information than X-ray powder diffraction. Fig. 2 shows the FTIR spectra of the samples as-synthesized. As can be seen from Fig. 2, the FTIR spectra of pure LTA (S–KF–0.1 and S–KF–1) and pure FAU (S–NaCl–0.002 and S–NaF–0.002) were consistent with the literature reports [21]. For pure LTA, the adsorption bands at 467 cm^{-1}, 669 cm^{-1}, and about 1000 cm^{-1} can be assigned to bending, symmetric stretching, and asymmetric stretching vibrations of internal tetrahedra, respectively. The adsorption band at 563 cm^{-1} is connected with vibrations of D4R, which are dominant sub-units in LTA structure. For pure FAU, the adsorption bands at 467 cm^{-1}, 669 cm^{-1}, and around 1000 cm^{-1} can be assigned to bending, symmetric stretching, and asymmetric stretching vibrations of internal tetrahedra, respectively, and the adsorption band at 758 cm^{-1} can be assigned to symmetric stretching vibrations of external linkages. The adsorption band at 567 cm^{-1} is connected with vibrations of D6R, which are dominant sub-units in FAU structure. For the LTA/FAU phase, with the decreasing of FAU fraction in the mixture the adsorption band at 758 cm^{-1} decreased and became a shoulder, and eventually disappeared for the pure LTA phase. Simultaneously, the adsorption band at 567 cm^{-1} gradually became wider and shifted to 563 cm^{-1} (Fig. 2(c)).

All of the stretching vibrations above mentioned are sensitive to framework Si/Al composition and shift to higher frequency with decreasing Al content [21]. However, no shift could be observed for these adsorption bands in the as-synthesized zeolites, indicating the Si/Al composition of the zeolites was not affected by the addition of salts. Based on the frequency of these stretching vibrations we could recognize that the FAU phase in the synthesized samples was zeolite X with lower Si/Al composition rather than zeolite Y with higher Si/Al composition. In addition, in zeolite Y the T–O bend near 467 cm^{-1} should contain a high-frequency shoulder but not present in X[21].

3.3. *Effect of cations and anions on the morphology of zeolites*

The ideal morphology of LTA crystal is a cube with sharp edges. Actually, the morphology of synthesized LTA crystal may usually be truncated cube or rounded cube depending on the condition of synthesis [7,8]. Fig. 3 shows

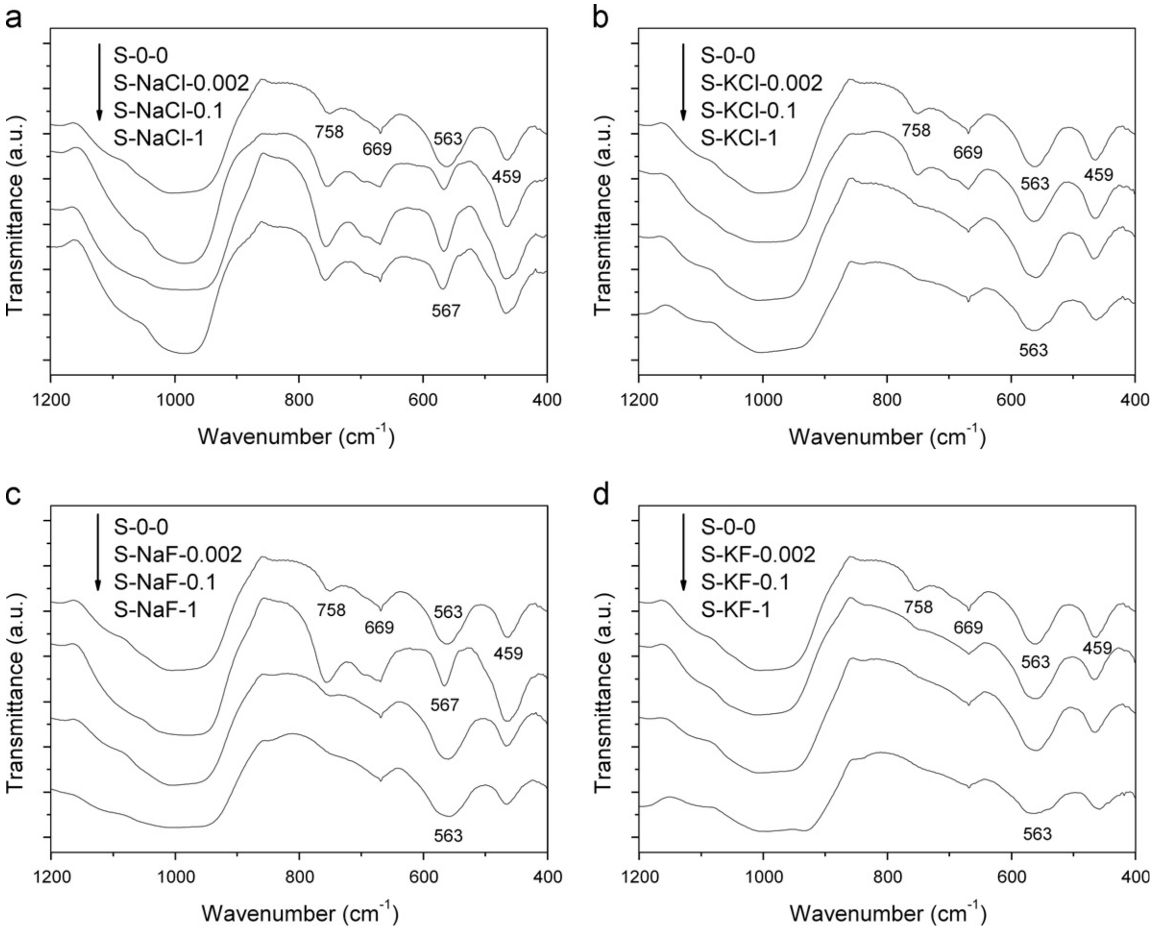

Fig. 2. FTIR spectra of the as-synthesized samples by adding (a) NaCl, (b) KCl, (c) NaF, and (d) KF.

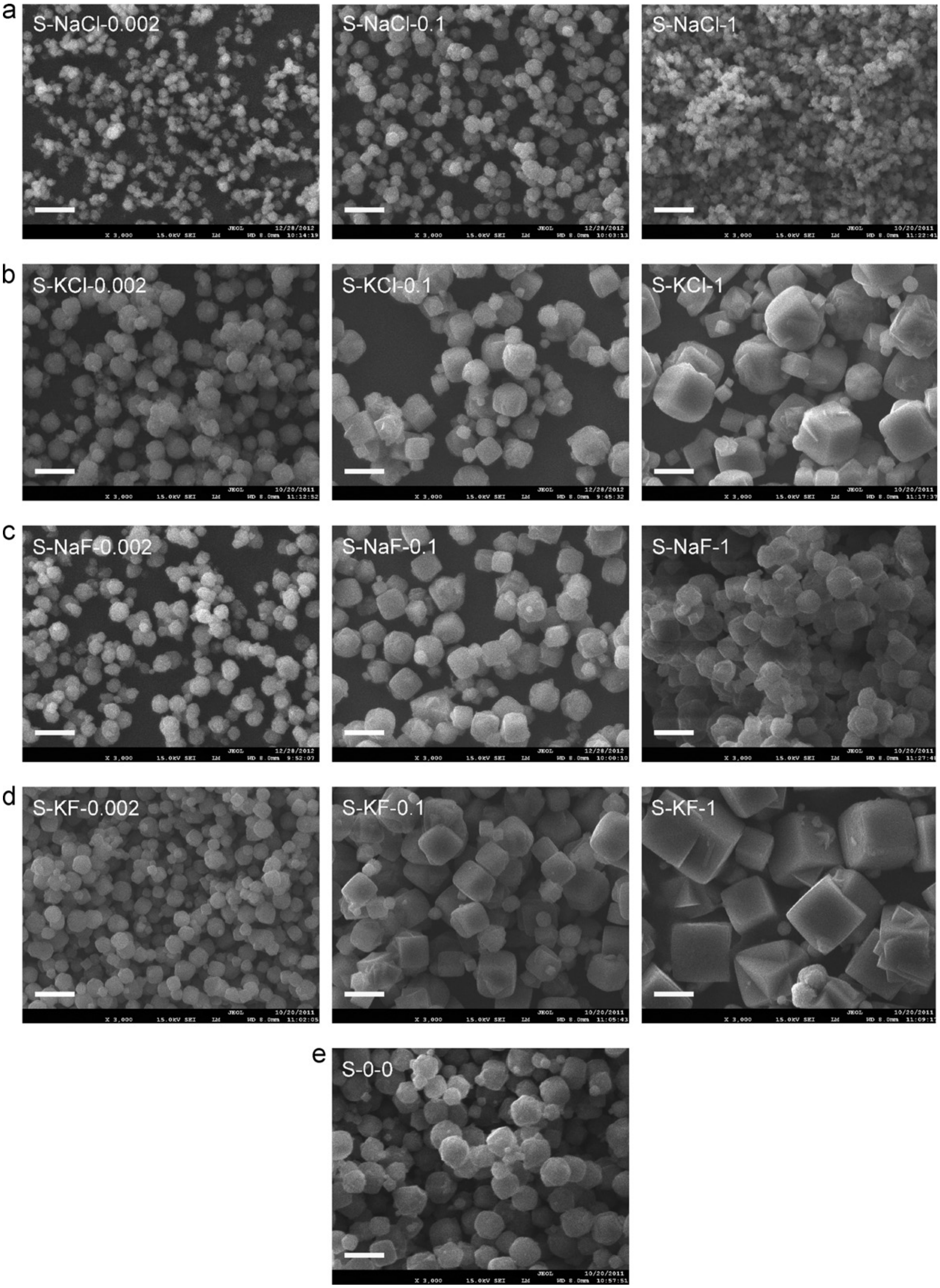

Fig. 3. SEM images of the as-synthesized samples by adding (a) NaCl, (b) KCl, (c) NaF, and (d) KF, and without adding salts (e). The scale bar is 5 μm.

the morphology of the products as-synthesized in this study. As can be seen, the sample S–0–0, which was synthesized from the initial mixture without the addition of salts, exhibited rounded cubic shape with the size of about 3 μm, though this sample was not pure LTA. The sample S–NaCl–0.002, S–NaCl–0.1, and S–NaCl–1, which were FAU zeolite, presented rough-surface globe with the size of only about 1 μm, 2 μm, and 1 μm, respectively, much smaller than S–0–0. The sample S–KCl–0.002, which was a mixture of LTA/FAU, was globe with the size of about 2.5 μm. The sample S–KCl–1 was mostly cubic with round edges which size was distinctly larger than that of S–0–0 and S–NaF–1, indicating K^+ suppressed the nucleation of LTA resulting in larger crystals. The sample S–NaF–0.1 and S–NaF–1 were similar to S–0–0 in the shape and size, implying that F^- concentration in this level did not influence the nucleation of LTA. The sample S–NaF–0.002 (FAU zeolite) was rough-surface globe with the size of only about 2 μm. The addition of KF significantly influenced not only the morphology but also the size of LTA crystal. With the increase of KF from $n=0.002$ to 1, the morphology changed from a cube with rounded edges to a cube with sharp edges, and the sizes of sample increased from about 2 μm to about 7 μm. These results further demonstrated the suppressing effect of K^+ on the nucleation of LTA.

3.4. *Mechanism of cations and anions on the phase selection of LTA/FAU zeolites*

Although there was no direct evidence of how the added ions react with the component of zeolite synthesis, based on above results, we still try to give an alternative interpretation of the added ions on the phase selection of LTA/FAU zeolites. As have known, 4R and D4R was proposed as the precursors of LTA. By the reactions with amorphous silica, 4R and D4R could transform to 6R and D6R, the precursors of FAU [22–25]. Because the transformation was slow, a long aging process at room temperature was usually considered necessary for the formation of pure FAU without LTA impurity [26]. In this study, without adding ions in the synthesis system LTA was dominant product, suggesting that little transformation of 4R and D4R to 6R and D6R occurred. The addition of Cl^- in the synthesis system may catalyze this transformation resulting in the nucleation and growth of FAU, which strongly inhibited the formation of LTA. Similar to Cl^-, F^- with a low concentration also catalyzed the transformation of 4R and D4R to 6R and D6R resulting in pure FAU product. However, F^- with higher concentration also favored the growth of LTA crystal, resulting in the production of LTA-rich phase or pure LTA phase. K^+ may inhibit the above transformation and decrease the competition of FAU with LTA. Meanwhile, the increase of K^+ also compressed the nucleation of LTA resulting in larger crystals.

4. Conclusions

We added different amounts of common inorganic salts NaCl, KCl, NaF, and KF into a standard LTA synthesis system and identified the influence of Cl^-, F^-, and K^+ on the phase selection of LTA/FAU by comparing the phase of zeolites obtained. The results showed that the addition of trace amounts of the salts could change the resulting zeolites. Moreover, the cations and anions of these salts can appear synergetic or antergic effects. Although studies on the effects of additives may be the most common topic in zeolite synthesis, the concentration of additives used is usually considerably high, thus the low-concentration effects of additives may be neglected. In our study, when $n=0.002$, the mole fraction of the salts added in the synthesis mixture was only about 1.5×10^{-5} calculated from the molar composition of the synthesis mixture ($3.165Na_2O:1.926SiO_2:Al_2O_3:128H_2O:nX$). To the best of our knowledge, it has not been reported that additives, especially common inorganic ions such as Cl^-, F^-, and K^+, with such a trace amount like this study can cause so strong effects on the phase selection of zeolites. Our finding not only provides a simple approach to control the phase of zeolites, but also calls attention to the significant effects of impurities on zeolite synthesis, especially when using natural materials or industrial waste as feedstock. However, the reaction mechanism of the added ions is not clear due to the lack of direct evidence. Future work therefore should include the elucidation of the mechanism as well as the investigation of more ions and more synthesis systems.

Acknowledgment

The support of research grants from the Research Center of New Catalytic Materials is gratefully acknowledged.

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