# Crystal growing of NaX type zeolite

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**Abstract**   A large NaX type zeolite crystal of a uniform particle size of 20 μm are grown with various $H_2O$ content by hydrothermal reaction and added seed crystal (2~3 μm) to reactant solution as a function of different adding seed levels from 3 to 15 %. The result that increased purity of NaX zeolite above 95 % and homogeneity of crystal size by increasing adding seed levels, also decreased crystallization time. It was explained that adding seed to synthesis solution leaded out increase of surface area for physical contact reaction and directed growth of seed crystal, so more rapid consumption of reaction gel as increase seeding levels.

## 1. Introduction

Zeolites are crystalline aluminosilicate with fully cross-linked open framework structures made up corner-sharing $SiO_4$ and $AlO_4$ tetrahedra. Each framework $AlO_4^{5-}$ tetrahedron bears a net negative charge which is balanced out by a counter cation [1, 2]. All these structures show the large internal voids, known as supercage or nanocages, characteristic of zeolites shapes and dimensions of these voids show a tremendous variety. However size and shape of the apertures linking these voids also play an important part in the determination of the zeolite properties, since the size of these windows determines what molecules can penetrate inside the zeolite. In sodalite, zeolite X has a much larger supercage; 13 Å cross, with window of 7.8 Å. The supercage of zeolite A is slightly smaller; 11.4 Å, but the windows are much smaller; 4.2 Å. These cages interlock to define a three-dimensional network [3-5].

NaX Zeolites are used to adsorb a moisture from a gas until saturated. This includes industrial applications because of their uniform large window size of 7.8 Å, structural and thermal stability. They can remove water to very low partial pressures and are very effective desiccants with a capacity of up to more than 25 % of their weight in water. This allows them to use a regenerative desiccant, that is to say a desiccant which may be used to absorb moisture from a gas until saturated, and may thereafter be heated to drive off absorbed water or pressure swing to remove adsorbed water to render the desiccant fit for re-use [6, 7].

Most of the synthetic zeolite by hydorthermal method are produced under non-equilibrium conditions and are considered, in a thermodynamic point of view, as metastable phase. According to the Ostwald rule of successive transformation, at long reaction times metastable molecular sieves recrystallize to other more stable structure under certain conditions [8, 9]. Crystalline NaX zeolite prepared under normal synthesis conditions is also too fine particle size from 0.5 to 1.0 μm to application in the cleaner technologies, In order to obtain optimal combination between zeolite and binder on the ceramic paper for dehumidifier rotor. We need a large crystal size about of 5~10 μm. The synthesis of zeolite is simple and at the same time complex. It is simple in the sense that usually only few chemical manipulations are required to synthesis most zeolite but complex in that there is little fundamental understanding in the processes during zeolite crystallization. This poor understanding of the complex crystallization process precludes the prediction of the method make large uniform crystals of NaX. It is our assessment that further experimental work is needed to establish the experimental conditions necessary to produce the required zeolite product with a reproducible yield and crystal size distribution. The experimental parameters which touch the crystallization of NaX exert and influence on the modification and size

of NaX. These parameters are methods and species of seed [10, 11]. The aim of this work should be expained more in detail the growth of NaX zeolite under the influence of different seed levels and different $H_2O$ contents.

## 2. Experimental

A NaX zeolite crystals of a uniform particle size of 5 μm were synthesized from the seed crystals (2~3) at levels of 3~15 % in a mother liquid having a composition of $4.12Na_2O : Al_2O_3 : 3.5SiO_2 : 593~2,000H_2O$ content by hydrothermal treatment. The reactant materials used are Ludox HS-40 colloidal silica (Aldrich chem. Co. Inc), NaOH (Junsei chem. Co.) and $NaAlO_2$ (Junesei chem. Co.). All of the required water for the batch is placed in the flask. All of the required sodium hydroxide was dissolved in this water with agitation. After the sodium hydroxide was completely dissolved, the required sodium aluminate was added and completely dissolved with agitation. The resulting solution was usually allowed to return to ambient temperature. The required amount of sodium silicate was then added slowly, with agitation. This reactant mixture was agitated for about 30 minutes. Next, the mixed gel solutions were placed 25ml teflon-lined autoclaves, sealed tightly, and placed in convection oven at $90^{\circ}C$ to react at autogeneous pressure. Sample of the heated mixture, crystallized at $90^{\circ}C$ for times raging from 1 day to 9 days, were taken. Autoclave were removed at predetermined times from the oven and quenched in cold water to stop the reactions. Crystallized samples were obtained by filteration and washed thoroughly with water before being dried at $100^{\circ}C$ overnight.

The samples were characterized by powder X-ray diffraction and Rietveld method (M18 XHF, Macscience) using Cu kradiation. Crystallinity was determined from the peak area between $2\theta = 3~40^{\circ}$. Morphology and size of the crystallites were determined from scanning electron microscopy (SEM) images taken with S-2700, Hitachi.

## 3. Results and discussions

In the solution crystallization mechanism, in general, nuclei form and grow in the liquid phase. The latter proposes that an non-equilibrium exists between the

solidgel phase and the solution, and that nucleation occurs in the solution. The gel dissolves continuously, and the dissolved species are transported to nuclei crystals in the solution. In addition to zeolite formation via either of the two transformations, there is an evidence to indicate that both types of transformation can sometimes occur simultaneously. In typical, the crystallization of zeolite divided in to three periods: a, b, and c, as shown in Fig. 1. Part a is the "induction period" during which crystalline nuclei from but no crystalline product is observed. The length of the induction period is reduced by adding crystal seeds to the initial mixture and by decreasing $H_2O$ content in mixture solution. During the growth period, b, crystal nuclei grow rapidly in size, Finally, during the period c, the crystallization is over, and the products may transform into a more stable phase requiring a longer reaction time [12].

Figure 1 shows the crystallinity of the zeolite during crystallization of an aluminosilicate gel of composition; $4.12Na_2O : Al_2O_3 : 3.5SiO_2 : 593H_2O$ at different seed levels. As seen from the Fig. 1. the crystallinity (%) of NaX zeolite increases strongly with increasing seed levels. That is, the induction period for the drawing nucleation and crystallization time are getting shorter with increasing seed content.

Figure 2 compares the yield curves for crystalline NaX zeolites, where crystallinity defined as the relative intensity of a given peak in the XRD pattern, is often used as a measure of zeolite yield. The relative intensity of NaX zeolite peak (2θ): $6.16^{\circ}$ increased abruptly often a crystallization period, in the place of abrupt decrease in the intensity of the broad peak, showing the crystallization of amorphous component to zeolite. But after alonger crystallization time, NaX
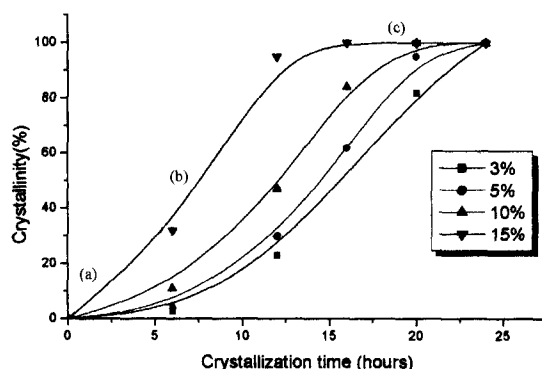


Fig. 1. Crystallization curves of synthesized NaX zeolite as a function of seed content.
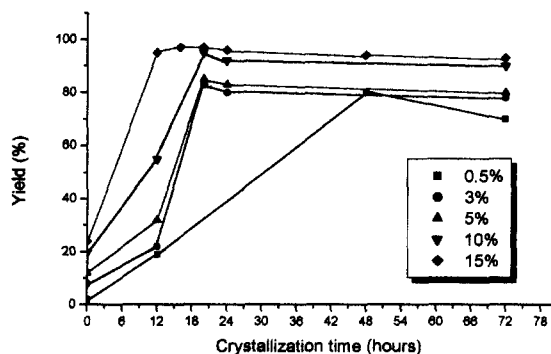
Fig. 2. Yield curves for synthesized NaX zeolite as a function of seed content.

zeolite recrystallized to other more stable structure, showing slightly decreased yield curves of NaX zeolite.

Figure 3 shows the SEM images of product at same crystallization time with different seed levels. The product in an induction period for the zeolite appeared to be an agglomerate of amorphous fine particles. The amorphous microparticles with increasing seed content

quickly were crystallized without appreciable change in size, with a resultant increase in the number of NaX crystal, as illustrated in Fig. 4 (mode 1). The other mechanism of crystallization, homogeneous crystal growth of NaX (mode 2 in Fig. 4).

In order to obtain a uniform crystal size of NaX zeolite and reduce the crystallization time, the initial reactant solution are produced by adding a different $H_2O$ content. Peak intensities were measured at given diffraction angles (2θ): $6.16°$ for NaX, $7.18°$ for NaA and $12.42°$ for P-type zeolite, respectively. The crystal of NaX zeolite is refer to as sodalite formed by $SiO_4^{4-}$ and $AlO_4^{5-}$ tetrahedra. When these sodalite units are joined by half of the six-member rings, zeolite X and zeolite Y of isostructure of NaX are obtained. The crystal of zeolite NaX is obtained the combined octahedra. The crystal of NaX zeolite octahedra was obtained by measurements on an scanning electron microscopy of "diameters" of the 10~15 μm crystals observed in the final crystallization with a different $H_2O$ content product after the different intervals of crystallization time from the start of heating. The crystal forms of NaX zeolite are octahedral showing rounded face in good
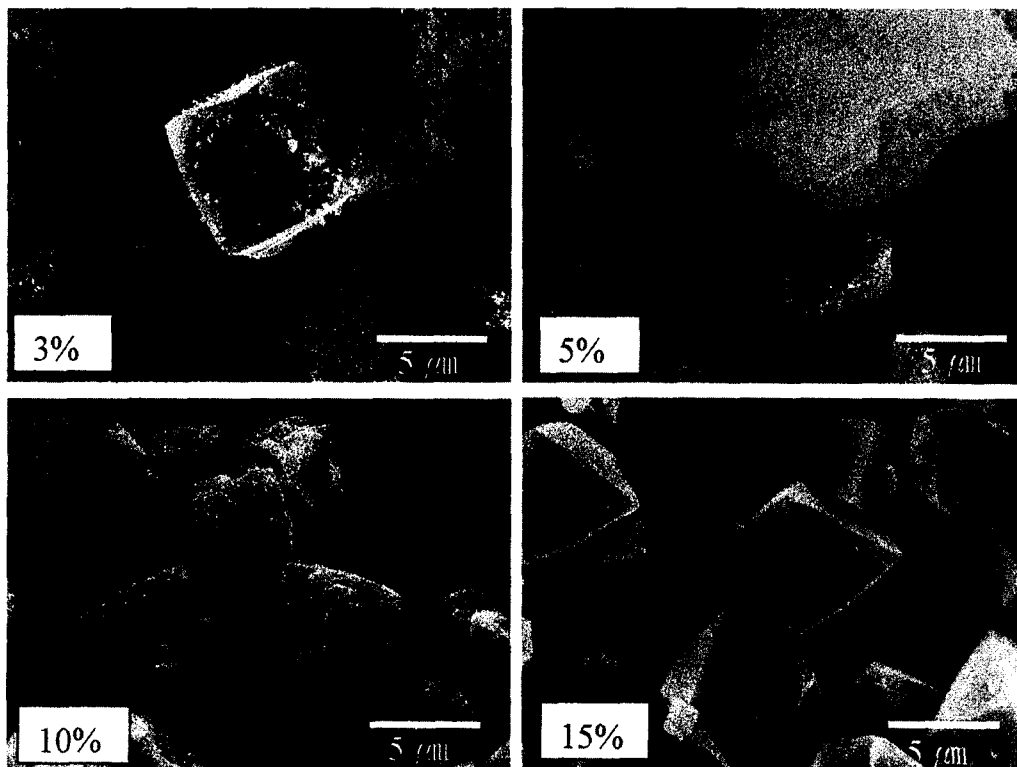


Fig. 3. SEM of synthesized NaX zeolite for 12 hours with different seeding level.

agreement with other authors [10] in Fig. 5. These rounded face are formed due to dissolving processes. Twins of NaX crystal can be observed clearly as well as overgrown on the surface of NaX zeolite. We observed also the co-crystalliztaion of mixed of different forms of NaA zeolite crystal with cubic form and
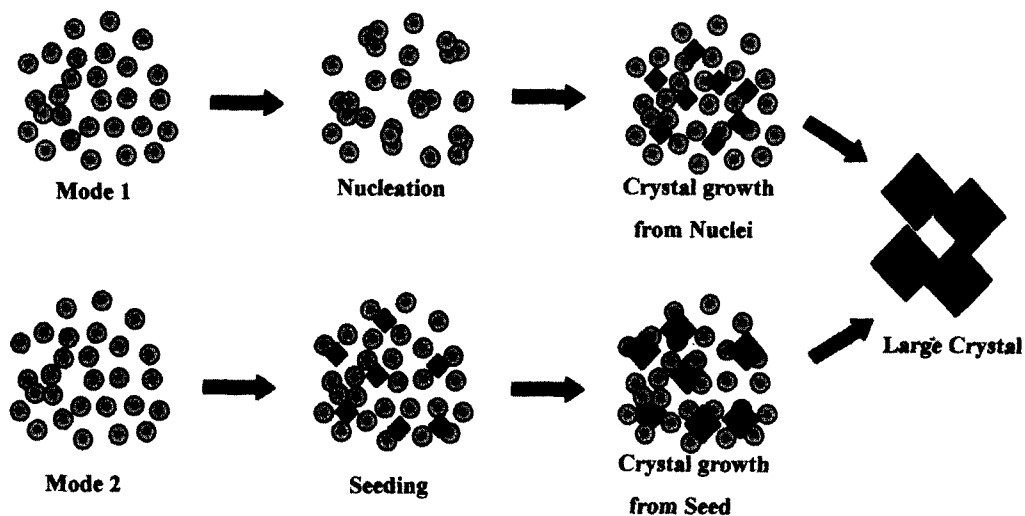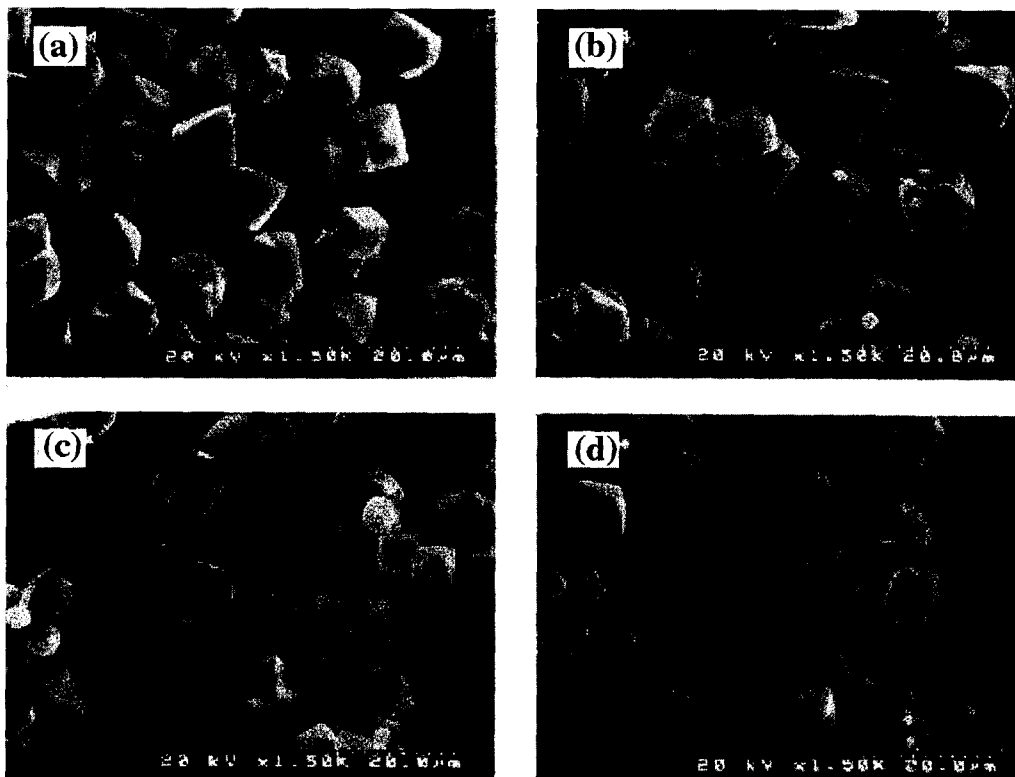


Fig. 4. Crystal growth model of zeolite.



Fig. 5. SEM images of NaX zeolite octahedra illustrating the influence of $H_2O$ content on crystal size. (a) in 1000 mole for 8 days (b) in 1000 mole for 12 days. (c) in 2000 mole for 18 days (d) in 2000 mole 24 days.
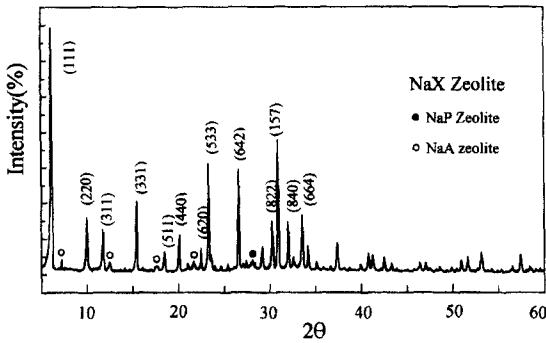
Fig. 6. XRD pattern of synthesis NaX zeolite for 8 days
with 1000 mole $H_2O$ by Rietveld method.



Fig. 8. The crystal size of NaX zeolite and crystal growth
rate with different $H_2O$ content.

NaP zeolite with round form from the gel for NaX-type composition having 1000 mole $H_2O$, respectively, which are detected by Rietveld method XRD, as shown in Fig. 6.

The influence of $H_2O$ content on the crystallinity of NaX zeolite from the same gel composition is showed by curves of Fig. 7. These curves describe the crystallization and the yield of NaX zeolite during the reaction using X-ray data. When comparing the crystallization curves with the different $H_2O$ content during the crystallization process, the induction period in 593 mol is 1 day, that in 1,000 mol is 3 days and that in 2,000 mol is 10 days, respectively. As seen in Fig. 8, during the so-called induction period when the gel remains amorphous in X-ray analysis. It takes place not only the formation of crystal nuclei but also their stationary growth. The absence of X-ray signs of crystallinity in this initial period of crystallization is not due to the absence of NaX crystals in the gel but to the small size of the crystals and to the insufficient reliability of the X-ray method for early stage of crys-
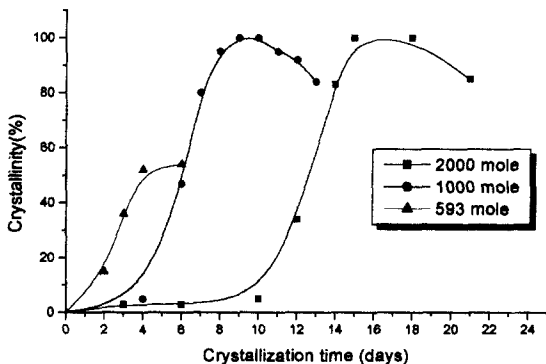
tal growth.

Figure 8. shows the crystal size growth of NaX zeolite during crystallization at different $H_2O$ content in a same gel composition. The $H_2O$ content in gel influence the rate of linear crystal growth, whereas the duration of crystallization determined by the times ($\tau_2$) 4 days, ($\tau_3$) 10 days and ($\tau_4$) 18 days and the size of crystals decrease with increasing $H_2O$ content. The linear growth rate determined from the relation $\Delta$ l/$\Delta$ t decrease strongly with increasing $H_2O$ content. It is 1.95, 1.36 and 0.53 $\mu$m/day for the $H_2O$ mol content of 593, 1,000 and 2,000, respectively. According to the increasing crystallization times, NaX zeolite was an increase in the upper size of 8 $\mu$m for 593 mol, 16 $\mu$m for 1000 mol and 9 $\mu$m for 2,000 mol $H_2O$ content in same gel.

## 4. Conclusions

The result of seeding resulted in the increase of crystal size compared with the unseeded batches and successfully lead to uniform size distribution of NaX. Crystallization of NaX with the seed of 15 % was completed in 12 hours without the existence of any other type of zeolite. It is postulated that seeding of the synthesis mixture creates sites, where crystal growth can occur immediately without the need for the nucleation of the synthesis gel.

The large amount of water in initial mixture not only reduces the degree of crystallization of NaX but also leads to an increase in large uniform crystals size in the final crystallization product. The decrease of the linear growth rate can be due to decrease of the product concentration of the silicate and aluminate ions in the gel liquid phase with increasing $H_2O$ content.



Fig. 7. Crystallization curves of synthesized NaX zeolite
as function of $H_2O$ content.

## Acknowledgments

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