

Nucleation, seeding and large crystal growth of NaX zeolite

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Large crystals of NaX zeolite of a uniform size of 50 μm were grown by a continuous crystallization method from seed crystals (10 μm) in a mother solution having a composition $3.5\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:2.1\text{SiO}_2:1000\text{H}_2\text{O}$. In order to grow crystals of zeolite X to an appropriate size by the continuous method, the mother solution was supplied into the starting solution with various seed contents (3~15 wt%) in an autoclave at 90°C after 7 days, 12 days, 16 days, 19 days and 24 days.

Key words: nucleation, seed, crystallization, large crystal, NaX zeolite.

Introduction

In recent years, zeolite crystals have been used in the chemical process industry as filters, adsorbents and catalysts for structured catalytic reactors because of their unique crystal structure, the microporous characteristics of zeolites, and their high chemical as well as their thermal stability [1, 2]. In order to improve existing catalytic and adsorbent processes, however, scientists need a better understanding of the structure of zeolites. Additionally, nearly perfect crystalline zeolite structures could be used as proton exchangeable membranes for fuel cells, which could result in major advantages over current separation and catalytic processes [4, 5], or as hosts for semiconductor clusters from ~1 to 20 nm in diameter to create electronic and optical properties specific to the form of "nanocrystals or quantum dots" [6]. However theoretically, it is difficult to synthesize uniform size NaX zeolites and to grow single phase large NaX zeolite crystals because crystal nuclei grow rapidly in size during the growth period and the products may transform into a more stable phase, for example, NaP, requiring a longer reaction time [7, 8] once the period the crystallization is over. For this reason, some scientists mentioned that it is impossible to grow synthetic zeolite single crystals to an appropriate size to analyze their structure [9, 10]. The aim of the present study should be explained in more detail as the growth of NaX zeolite under the influence of different H_2O levels, seed contents and reaction temperatures by a continuous crystallization method from

seed crystals (10 μm) in the mother liquid having a composition $3.5\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:2.1:\text{SiO}_2:1000\text{H}_2\text{O}$.

Experimental

NaX zeolite seed crystals of a uniform particle size of 10 μm were synthesized by a hydrothermal method in a mother liquid having a composition of $3.5\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:2.1\text{SiO}_2:1000\text{H}_2\text{O}$ as described in detail elsewhere [8]. The reactant materials used were Ludox HS-40 colloidal silica (Aldrich chem. Co. Inc), NaOH (Junsei chem. Co.) and NaAlO_2 (Junsei chem. Co.). In order to investigate the crystals grown by this continuous method, the mother solution was supplied continuously into an autoclave having a composition of $3.5\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:2.1\text{SiO}_2:1000\text{H}_2\text{O}$ with various seed contents after 7 days, 12 days, 16 days, 19 days and 24 days at 90°C and after 7 days and 9 days at 100°C. Figure 1 shows the autoclave with facilities to draw out the solution and

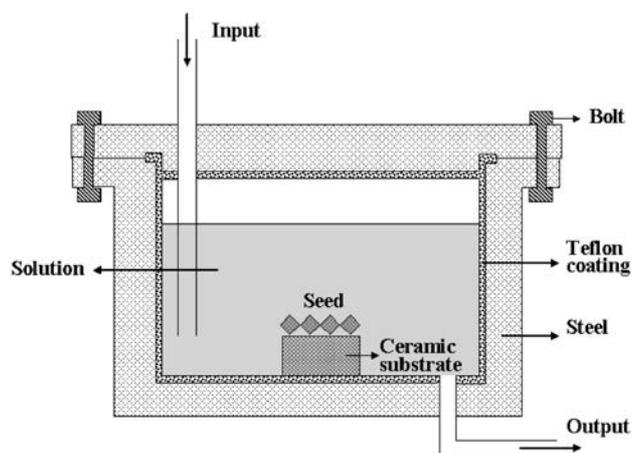


Fig. 1. Schematic diagram of autoclave.

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supply the same solution. The autoclave was removed at predetermined times from the oven and quenched in cold water to stop the reactions. Crystallized samples were obtained by filtration and washed thoroughly with deionized water before being dried at 100°C overnight. The BET technique was used to calculate the surface area of synthesized zeolite using a micromeritics ASAP 2010. The grown NaX zeolite crystals were characterized by powder X-ray diffractometry (XRD; Model RAD-2B, Rigaku Co., Tokyo, Japan) with CuK α radiation and by scanning electron microscopy (SEM; Model JXA-840, JEOL Co., Tokyo, Japan). The chemical composition of the zeolite was measured by X-ray fluorescent spectrometry (Model 3070, Rigaku Co., Tokyo, Japan).

Results and Discussions

The effect of H₂O and reaction temperature

In the solution crystallization mechanism, in general, nuclei form and grow in the liquid phase. It was proposed that an equilibrium exists between the solid-gel phase and the solution, and that nucleation occurs in the solution. The gel dissolves continuously, and the dissolved species are transported to primary nuclei crystals by the solution itself, either strictly within the solution, as in homogeneous nucleation, or catalyzed by extraneous material in the solution, as in heterogeneous nucleation. Secondary nucleation is catalyzed by the presence of parent crystals of the same phase, and occurs with a lower activation energy than primary nucleation [11].

Nucleation and crystallization typically are governed by a driving force related to the supersaturation and reaction temperature under the autogenous pressures. The influence of the reaction temperature on the crystallization of zeolite from the gel with the following mole ratio; 3.5Na₂O:Al₂O₃:2.1SiO₂:593~2000 H₂O (a) and with different H₂O contents (b) is illustrated by curves of Fig. 2, respectively. The curves describe the growth in mass of crystals during the gel crystallization using X-ray data. The characteristic S-shaped crystallization curve of zeolite in Fig. 2(a) and (b) can be divided into three periods: I, II, and III. Part I is the "induction period", during which crystalline nuclei form but no crystalline product is observed. The length of the induction period is reduced by the higher reaction temperature of 100°C in Fig. 2(a) and lower H₂O concentration of 593 mol in the gel as shown in Fig. 2(b). During the growth period, II, crystal nuclei grow rapidly in size. Finally, during period III the crystallization is over after 6 days in 593 mol, 9 days in 1000 mol and 17 days in 2,000 mol of H₂O, respectively. The complete crystallization completion of samples having 1,000 and 2,000 mol of H₂O after 9 and 17 hours reaction times showed slightly smaller yield curves of NaX zeolite about 10%, respectively. Because the product

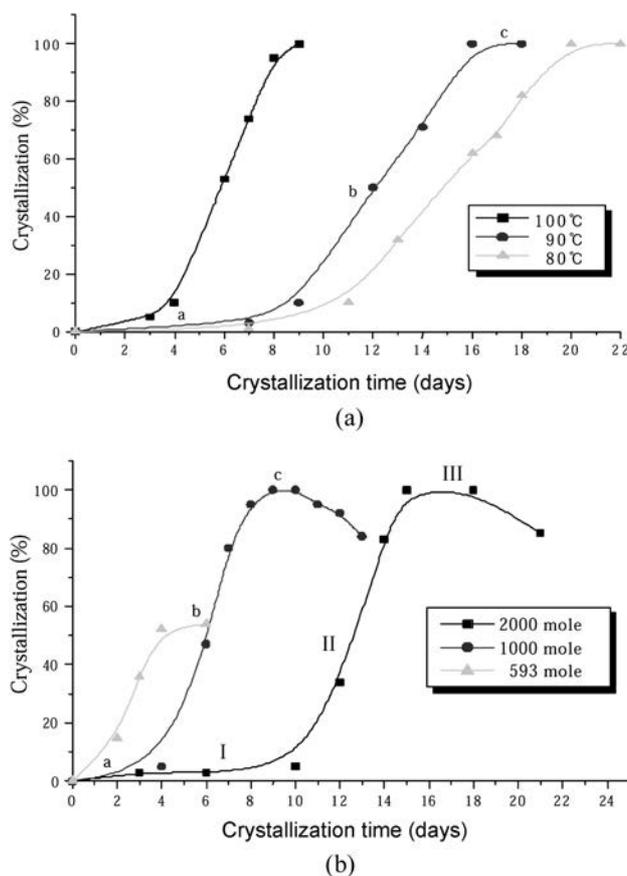


Fig. 2. Crystallization curves of NaX zeolite as a function of reaction temperatures (a) and H₂O contents (b).

of NaX was transformed into the more stable NaP type zeolite (detected by XRD), a spheroidal form having Na₂O:Al₂O₃:2.0-5.0SiO₂:5H₂O which has a high flexibility of Si-Al linkage in the framework. These structural distortions of this framework due to twinning, pseudo-systemary and was formed extra disorder lead to problems in growing large zeolite crystals and in determining their structures [12].

A smaller crystal size in the final crystallization product at 100°C as shown in Fig. 3(c) is the result of a high reaction temperature with the same gel which permitted one to conclude that the effect of reaction temperature is on the development of nucleation in the aluminosilicate gel at the higher temperature. Zeolite crystallization from aluminosilicate gels is well known to increase with increasing temperature and increasing alkali concentration in the gel.

The effect of seeding

In general, the result of seeding was an increase in the upper size of crystals compared with unseeded batches, as shown in Fig. 3(a) and (b). It is postulated that the seeding of the synthetic mixture creates sites where crystal growth can occur immediately without the need for nucleation of the synthetic gel. The crystal size only increased when the seeds were in direct

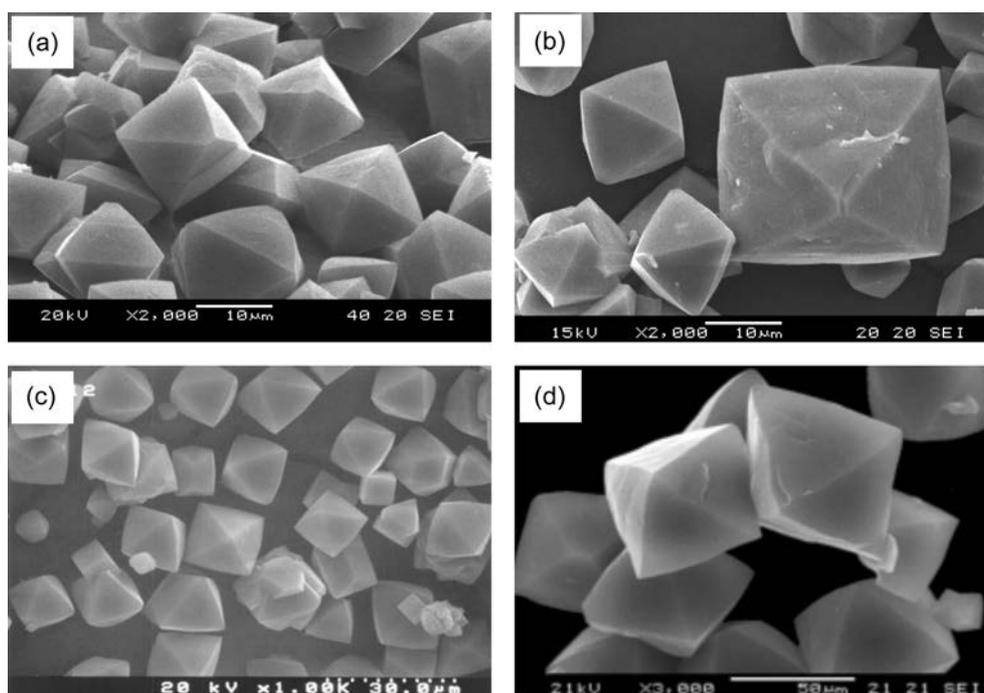


Fig. 3. SEM image of crystal growing of NaX zeolite by continuous crystallization method. (a) crystal at 90 °C for 7 days. (b) 7 days with 3% seed content at 90 °C. (c) crystal at 100 °C for 7 days. (d) 28 days with 10% seed at 90 °C.

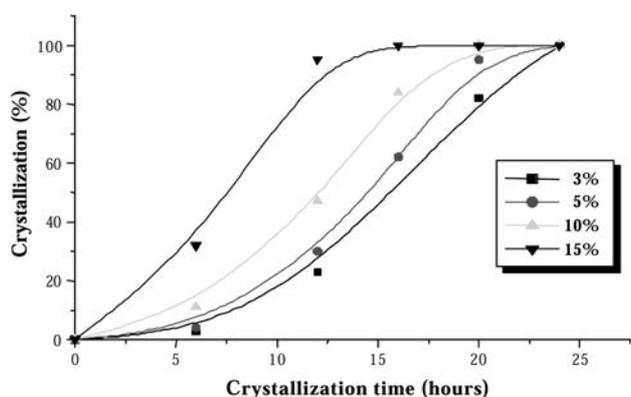


Fig. 4. Crystallization curves of NaX zeolite as a function of seed contents.

physical contact with the synthetic gel. But in the synthetic gel was also produced the self-induced nucleation particle which did not have direct physical contact with seeds and then showed a decrease in homogeneity of

the total crystal size in the final products, as shown in Fig. 3(b). Furthermore, adding seed crystals to a crystallization process has typically resulted in increased “crystallization” rates, as shown in Fig. 4. The enhanced rate might be due simply to increasing the rate at which solute is integrated into the solid phase from solution due to the increased available surface area, but also might be the result of enhanced nucleation of new crystals. The secondary nucleation mechanism referred to as initial breeding results from microcrystalline dust being washed off seed crystal surfaces in a new synthetic batch, and has been reported in zeolite systems [13]. These microcrystalline fragments grow to observable sizes, and result in greatly enhanced crystallization rates due to the significantly increased crystal surface area of 561 m²/g (15% seed content) compared to the unseeded system (480 m²/g), as shown in Table 1. Consequently, it is to be expected that addition of seed crystals to a synthetic system will introduce sub-micrometre sized crystallites into the system which will serve

Table 1. BET of Synthesized NaX zeolite

Sample name		Analysis data			
Seed content (%)/ reaction time	NaX yield (%)	single point BET (m ² /g)	multi point BET (m ² /g)	Pore volume (cc/g)	Average pore radius (Å)
15/12h	>95	561	532	0.308	11.65
15/72h	90	519	488	0.289	11.84
3/27h	80	494	461	0.272	11.82
0/120h	>95	480		0.262	12.50
NaP	-	7.2	7.3	0.032	88.34

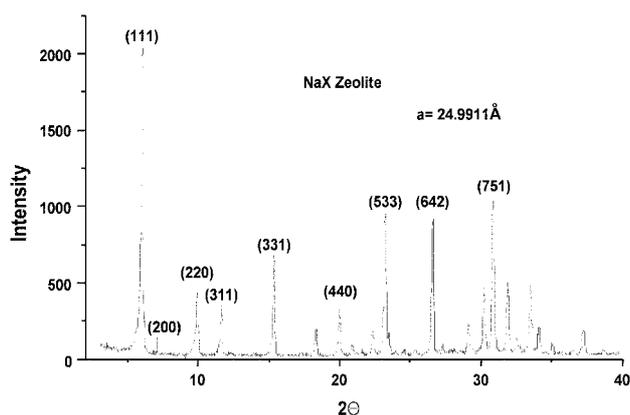


Fig. 5. Calculate lattice constants from peak locations and Miller indices of NaX Zeolite synthesized at 90°C for 7 days.

as nuclei.

As seen from the Fig. 4, the crystallinity (%) of NaX zeolite increases strongly with increasing seed contents. That is, the induction period for the nucleation and crystallization time gets shorter with increasing seed content. This makes it possible to conclude that the seed crystals played a direct role in increasing the crystal size and homogeneity of final products. The grown crystal morphology of NaX from a top view image shows that an octahedron is formed composed of 8 equilateral triangles. These triangle-shaped faces intersect all 3 crystallographic axes at the same distance, and thus the from notation of {111} in Fig. 3. The XRD patterns of this morphology showed only the NaX crystalline phase which has an average lattice constant $a=24.9911 \text{ \AA}$ with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 2.1~2.4, which was determined by XRF and XRD in Fig. 5.

Crystal growing by continous crystallization

Figure 6 compares the crystallization curves for crystalline NaX zeolites by a normal hydrothermal method with the continuous crystallization curves, where crystallinity defined as the relative intensity of a given peak in the XRD pattern, is often also used as a measure of zeolite yield. The XRD patterns were measured at given

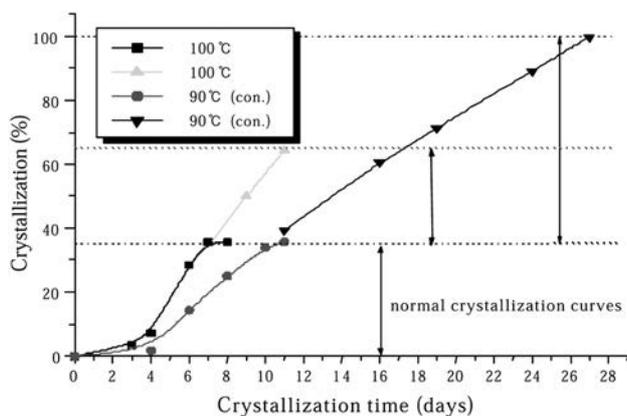


Fig. 6. Extended crystallization curves of NaX zeolite.

diffraction angles (2θ): 6.16°, 12.5° and 28.0° for NaX and NaP zeolites, respectively. The relative intensity of NaX zeolite peak at 6.16° increased abruptly after an induction period, in place of an abrupt decrease in the intensity of a broad peak, showing the recrystallization of an amorphous component to zeolite. The crystallization of zeolite increased abruptly with increasing reaction time, showing the transformation of NaX into NaP zeolite and also slightly decreased crystallization curves of NaX zeolite as shown in Fig. 2(b) in the normal crystallization process after 7 days at 100°C and 11 days at 90°C, respectively.

The influence of continuous crystallization on the crystal growing of NaX zeolite from the same gel composition at different temperature is shown by curves in Fig. 7. These curves describe the crystal size and also the crystallization of NaX zeolite during the reaction using X-ray data. By comparing the crystallization curves of the extended crystallization with that of the normal hydrothermal method during the crystallization process, the growing period of NaX zeolite can be extended from 11 to 28 days at 90 °C and from 6 to 10 days at 100 °C, respectively. As seen in Fig. 7, during the so-called crystal growing period, the crystal size of NaX shows stationary crystal growth. Most crystallization processes involve assimilation of material from solution via a growth process which can be described by the relation: $dL/dt = G = Ks^a$ where a is an exponent expressing the dependence of the linear crystal growth rate, G , on the supersaturation, s , and K is a temperature-dependent rate constant. The value of a will be 1.0 for diffusional transport limitations to a planar crystal surface, and between 1-2 for most surface reaction - limited growth processes [14].

The linear growth rate of zeolite crystallization from the starting aluminosilicate gel determined from the relation $k = dL/dt$ increases strongly with increasing temperature. It was 0.0441, 0.0595 and 0.0972 $\mu\text{m/h}$ for the reaction temperatures 80, 90 and 100 °C, respectively. From the Arrhenius plot the activation energy of the growth of NaX zeolite was found to be 43.2 kJ/mol.

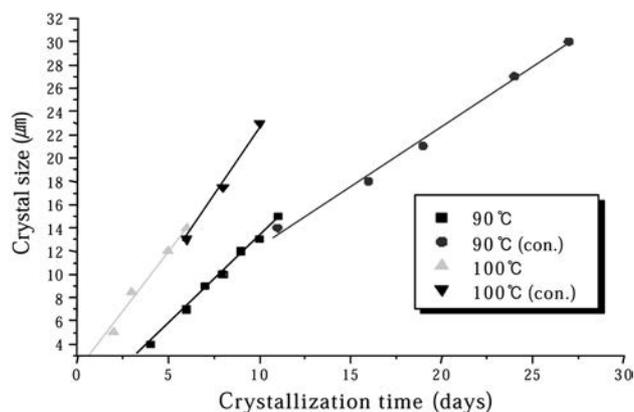


Fig. 7. Crystal size of NaX zeolite as a function of continuous crystallization time.

This value is considerably below the value of 62.5 kJ/mol obtained for NaX zeolite in Ref [15]. The crystal morphology of NaX zeolite octahedra obtained by SEM show a size of an average 50 μm and 38 μm observed for the 27 days crystallization at 90 °C and the 10 days at 100 °C, respectively.

Conclusions

A feeding mother liquid having seeds of a size of 10 μm resulted in an increase in the fraction of large crystals compared with unseeded batches and successfully led to large NaX zeolite crystals of 50 μm by a continuous crystallization method. It was postulated that the seeding in the synthetic mixture leads to an increase of surface area for physical contact, which encourages the reaction and directed growth of seed crystals without nucleation in the synthetic gel.

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