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Crystal growing and reaction kinetic of large NaX zeolite crystals

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Abstract

Large crystals zeolite NaX with a uniform size of 50 μm were grown by a continuous crystallization method from seed crystals (10 μm) formed in a mother solution with the $3.5Na_2O:Al_2O_3:2.1SiO_2:1000H_2O$ composition. In order to grow zeolite NaX crystals to an appropriate size by the continuous method, the mother solution was fed into an autoclave a solution with various seed contents (3–20 wt.%); the autoclave has at 90 °C and the solution was added after 7, 12, 16, 19 and 24 days or at 100 °C after 7 and 9 days. The morphology of NaX zeolite crystals when viewed from the top shows an octahedron that is formed from eight equilateral triangles. These triangular faces intersect all three crystallographic axes at the same distance having an average lattice constant $a = 24.9911$ Å and a SiO_2/Al_2O_3 molar ratio of 2.1–2.4. The activation energy for growth of NaX zeolite crystals was found to be 43.2 kJ/mol.

Keyword: Precursors-organic; Optical microscopy; X-ray methods; Fuel cells; Zeolite

1. Introduction

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 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, potentially offering major advantages over current separation and catalytic processes.[3,4] They could also be employed as hosts for semiconductor clusters from ∼1 to 20 nm in diameter to create electronic and optical properties specific to the form of nano-crystals or quantum dots.[5] Theoretically, it is difficult to synthesize uniform size NaX zeolite crystals or to grow single phase, large NaX zeolite crystals, because the crystal nuclei grow rapidly during the growth period. Furthermore, the product may transform into a more stable phase, such as NaP.[6] For this reason, some scientists contend that it is impossible to synthesis large, single-phase zeolite crystals to an appropriate size so as to analyze their structure.[7]

The aim of this study was to study the growth of large NaX zeolite crystals under the influence of different H_2O content and seed content in the synthesis solution, or at a various reaction temperature by continuous crystallization method using seed crystals.

2. Experimental

NaX zeolite seed crystals of a uniform particle size of 10 μm were synthesized by the hydrothermal method in a mother solution having a composition of $3.5Na_2O:Al_2O_3:2.1SiO_2:1000H_2O$ at 90 °C for 7 days. 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 introduced continuously into an autoclave a starting solution of the $3.5Na_2O:Al_2O_3:2.1SiO_2:1000H_2O$ composition with various seed contents after 7, 12, 16, 19 and 24 days at 90 °C and after 7 and 9 days at 100 °C. The autoclave was removed at predetermined times from the oven in order to arrest the reactions. Crystallized samples were obtained by filtration and washed thoroughly with deionized water before being dried at 100 °C overnight. A micromeretics Accelerated Surface Area and Porosimetry (ASAP 2010) instrument was used to determine the surface area of the synthesized zeolite crystals. A semiquantitative chemical analysis performed to estimate the SiO_2/Al_2O_3

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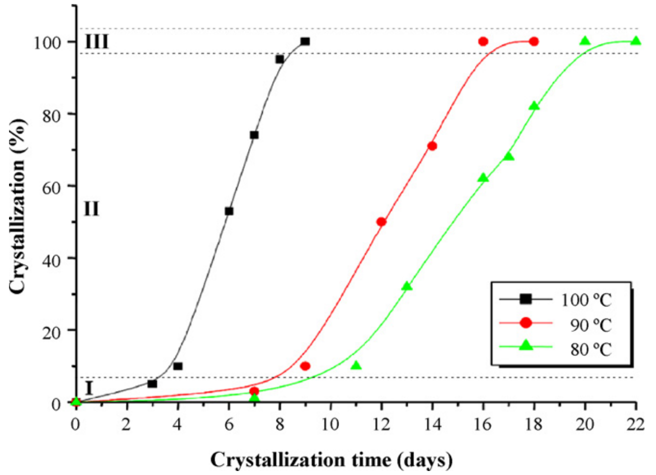

Fig. 1. Crystallization curves of NaX zeolite as a function of the reaction temperature.

ratio was carried out via fluorescent X-ray spectrometry (Model 3070, Rigaku Co., Tokyo, Japan). The grown NaX zeolite crystals were characterized by powder X-ray diffractometry (XRD; Model RAD-2B, Rigaku Co.) with Cu Kα radiation and by scanning electron microscopy (SEM; Model JXA-840, JEOL Co.). The chemical composition of the zeolite was measured by X-ray fluorescent spectrometry (XRF, Model 3070, Rigaku Co.).

3. Results and discussion

3.1. The effect of reaction temperature

Nucleation and crystallization in the solution are typically governed by a driving force related to the supersaturation and reaction temperature under the autogenous pressures. Fig. 1 shows the influence of the reaction temperature on the crystallization of zeolite from the gel with the following mole ratio; $3.5Na_2O$:Al_2O_3:$2.1SiO_2$:$1000H_2O$. The curves describe the growth in mass of crystals during the gel crystallization, as obtained from XRD data. The characteristic S-shaped crystallization curve of the zeolite can be divided into three periods. During the induction period (I), crystalline nuclei form but crystalline product is not observed by XRD.[8] The length of the induction period is reduced by a higher reaction temperature of 100 °C. During the crystallization period (II), crystal nuclei grow rapidly in size. Finally, during the stable period (III), the crystallization is over after 8 days at 100 °C, 15 days at 90 °C and 20 days at 80 °C, respectively.

The smaller crystal size of the final product at 100 °C compared to 90 °C for 7 days permits to conclude that the reaction temperature influences the zeolite nucleation in the aluminosilicate gel. Zeolite nucleation from aluminosilicate gels is well known to increase with increasing temperature and increasing alkali concentration in the gel.[9]

3.2. The effect of seeding

In general, adding seed crystals to a crystallization process taking place in solution has resulted in increased crystallization rates, as shown in Fig. 2. That is, the necessary time for nucleation and crystallization became shorter with increasing the seed content. This leads to the conclusion that the seed crystals played a direct role on the crystallization rate and homogeneity of final products. The enhanced crystallization rate might be caused by the increased rate with which solute is integrated into the solid, crystalline phase due to the increased available surface area, but might also be the result of enhanced nucleation of new crystals (secondary nucleation). The secondary nucleation mechanism referred to as initial breeding results from microcrystalline dust being washed off from the seed crystal surfaces in a new synthetic batch, and has been reported in zeolite systems.[10,11] These microcrystalline fragments grow to observable sizes, and result in greatly enhanced crystallization rates due to the significantly increased crystal surface area of 542.36 m^2/g (10% seed content) when compared to the unseeded system (284.56 m^2/g) as shown in Fig. 2.

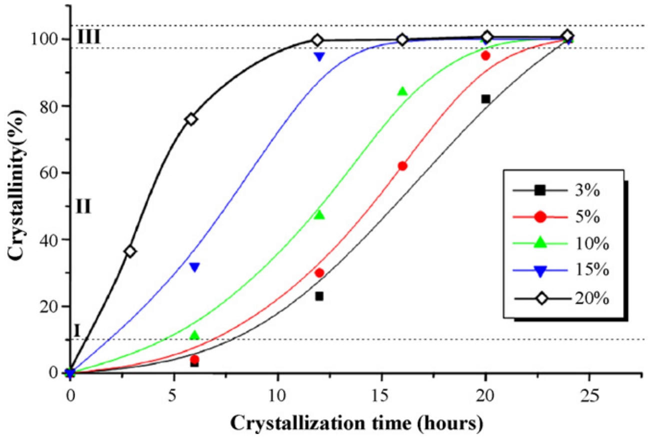

Fig. 2. Crystallization curves of NaX zeolite as a function of the seed content.

Consequently, it is to be expected that the addition of seed crystals to a synthetic solution will introduce sub-micrometer crystallites into the system that will serve as nuclei. The crystal size was only increased when the seeds were in direct physical contact with the synthetic solution. Moreover, in the synthetic gel new crystals nucleated that did not have direct physical contact with the seeds and that lead to a decrease in the homogeneity of the total crystal size in the final products, as shown in Fig. 3(a)–(c). 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 morphology of NaX crystal when viewed from the top shows an octahedron that is formed from eight equilateral triangles. These triangular faces intersect all three crystallographic axes at the same distance as shown in Fig. 3. The XRD patterns of these crystals revealed only the NaX crystalline phase, which has an average lattice constant $a = 24.9911$ Å and a SiO_2/Al_2O_3 molar ratio of 2.1–2.4, as was determined by XRF.

3.3. Continuous crystallization

Fig. 4 shows the influence of continuous crystallization on the crystal growth of NaX zeolite from the same gel composition at

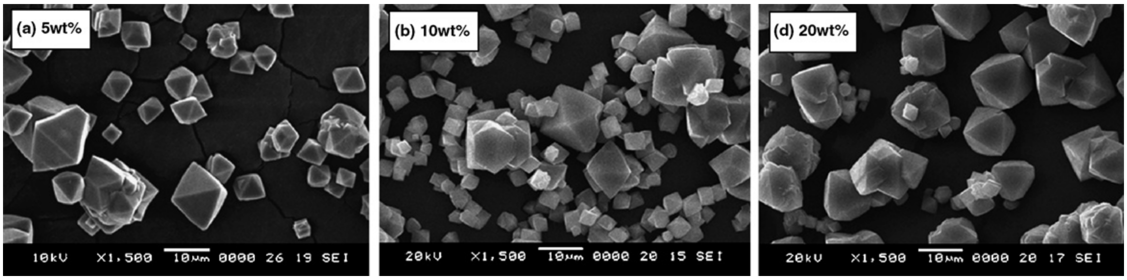

Fig. 3. SEM images of NaX zeolite as a function of seed.

different temperature. These curves describe the crystal size and also the crystallization of NaX zeolite during the reaction using SEM and XRD data. Comparing the crystallization curves of the extended crystallization with that of the normal hydrothermal method reveals that 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.

3.4. Reaction kinetic of crystal growth

In general, during the so-called crystal growing period, the crystal size of NaX shows a 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 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 and 2 for most surface reaction-limited growth processes.[12]

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 µm/h for a reaction temperature of 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. This activation energy was calculated from Eqs. (1) and (2):

$$K\ (\mu\text{m/h}) = \frac{\Delta l}{\Delta t} \tag{1}$$

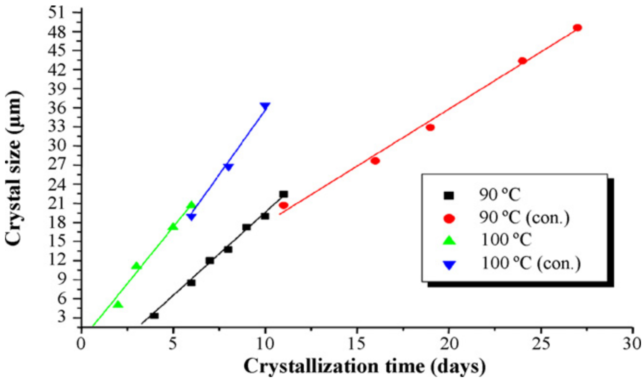

Fig. 4. Crystal size of NaX zeolite as a function of continuous crystallization time.

$$\ln K = -\frac{E_a}{RT} + \text{const.} \tag{2}$$

where K is the reaction rate, Δl the change of crystal size (µm), Δt the change of reaction time (h), R the universal gas constant (8.314 J/mol K), T the absolute temperature (K), and E_a is the activation energy (kJ/mol).

This value is considerably below the value of 62.5 kJ/mol reported for NaX zeolite.[13] SEM investigation reveals that the NaX zeolite octahedra have an average 50 and 38 µm after 27 days crystallization at 90 °C ore 10 days at 100 °C, respectively.

4. Conclusions

NaX zeolite crystals of 50 µm were successfully grown by a continuous crystallization with seed crystal. The seeded crystal morphology of NaX zeolite shows that an octahedron is formed composed of eight equilateral triangles which has an average lattice constant of 24.9911 Å with a SiO_2/Al_2O_3 molar ratio of 2.1–2.4. The activation energy for growth of NaX zeolite was found to be 43.2 kJ/mol.

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