

Crystal Growth of NaX Zeolite in Aluminosilicate Gels

Ik-Jin Kim, Jong-Pil Ha, Seon-Myoung Kang, Dong-Nam Seo*,
Mi-Jeong Jung**, In-Ho Moon**

*Institute for Processing and Application of Inorganic Materials, PAIM,
Dept. of Material Science and Engineering, Hanseo Uni., Seosan, 356-820, Korea*

** Dept. of Chem., Hanseo Uni., Seosan, 356-820, Korea*

*** Shingsung ENG Co, Ltd., Ansan, 425-090, Korea*

1. Introduction

A zeolite is a crystalline aluminosilicate with an open framework structure based on an extensive three dimensional network of oxygen ions. Saturated with the tetrahedral sites formed by the oxygen can be either a Si(+4) or an Al(+3) ions. Most of zeolites used commercially are produced synthetically. Zeolites have void space (cavities or channels) that can host cations, water or other molecules. Because of their regular and reproducible structure, they behave in a predictable fashion.

The SiO_4 are neutral: $\text{Si}^{+4}/4\text{O}^{-1}$ but the AlO_4 results in a net negative charge: $\text{Al}^{+3}/4\text{O}^{-1}$. The net negative charge is balanced by cations that are present during the synthesis. In natural zeolites, the most common cations are Na^+ and Ca^+ ; These cations reside within the three-dimensional network. They are easily traded in for other ions by ion exchange; this is another one of the characteristic zeolite properties. Through ion exchange, other metal ions can be introduced; this might influence the pore size, thereby modifying the molecular sieving or catalytic properties of the zeolite, or promote intersystem crossing.

NaX Zeolites are used to adsorb a moisture from a gas until saturated. This includes applications of industrial importance because of their catalytic, sorptive, and ion-exchange properties, drying, purification and separation. Especially, 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. and NaX crystals are used as 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.

A method of preparing larger crystals of the zeolite NaX was the hydrothermal formation. Basing on this procedure, we investigated detailed factors which influence the crystallization process considering chemical and crystallographic approaches to the problem. The number of factors operating in the NaX system is larger and renders more difficult to assign the experimental parameters to nucleation or crystal growth.

The aim of this work was to study the growth of NaX zeolite under the influence of different experimental composition and seed method conditions. In this study, we present our result dealing especially with the crystal growth of NaX zeolite.

2. Experimental

A large number of interrelated parameters may contribute to the synthesis of a particular zeolite including ; gel composition and concentration, reaction temperature and time, pH, the presence of organic additives and mineralizers, agitation, crystals, etc. The quantities of ingredients required for the desired oxide mole ratios in the initial reactant composition are determined. Starting reactant materials with composition of $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O} = 5.0 : 1.0 : 3.9 : 160$ for NaX were prepared by hydrothermal treatment. Schematic diagram of the preparation and crystal growth of NaX zeolite is shown in Fig. 1. 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 is agitated for about 30 minutes and is then allowed to digest quiescently at ambient temperature for 1 day. Next, the mixed gel solutions were placed 25ml Teflon-lined autoclaves, sealed tightly, and placed in convection oven at 90°C to react at autogeneous pressure. Sample of the heated mixture, crystallized at 90°C for times ranging 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 filtration and washed thoroughly with water before being dried at 100°C overnight. Products were then examined by powder X-ray diffraction (XRD) to determine the identity and degree of crystallinity of any zeolitic phase present. Several of the products were also examined by scanning electron microscopy (SEM).

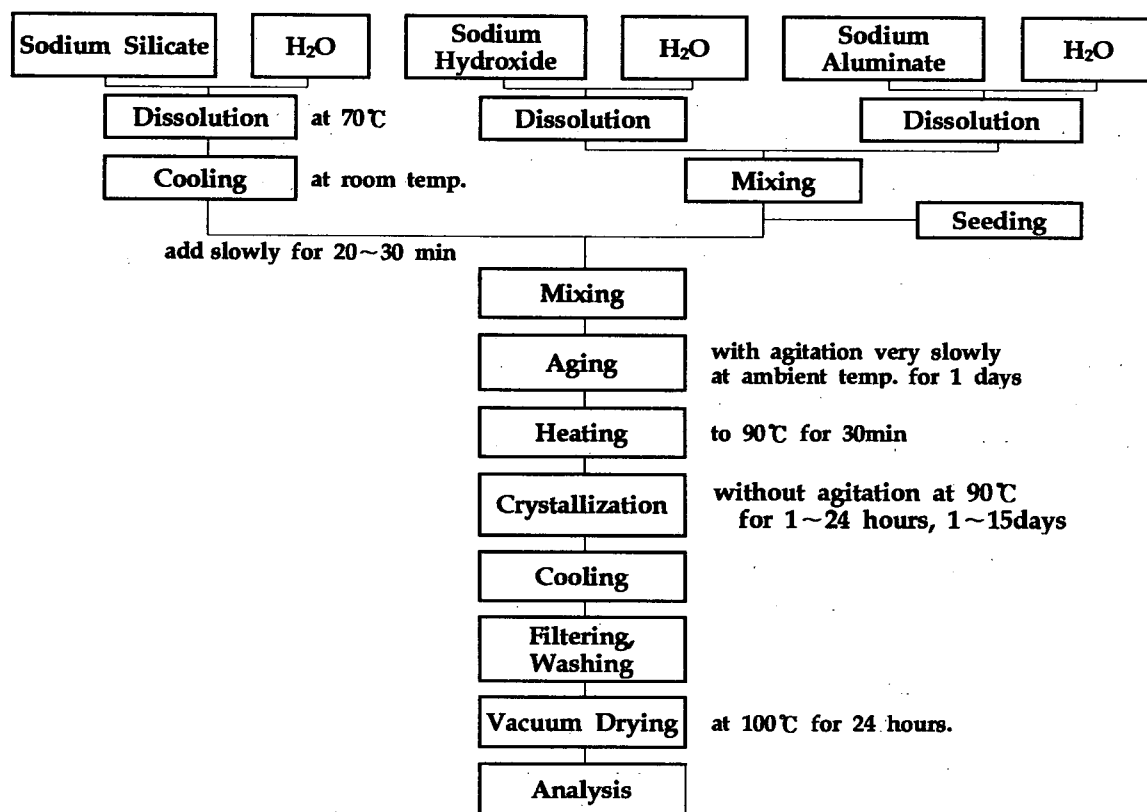


Fig. 1. Flow chart for zeolite synthesis.

3. Results and Discussion

We have investigated the effect of seed method such as zeolites X can be formed from the same synthesis mixtures. We have also studied how crystallization time influence crystal size. XRD patterns were recorded on a MXP-18 system using $\text{CuK}\alpha$ radiation. Peak intensities were measured at given diffraction angles (2θ): 6.16° , 12.5° , and 24.3° for NaX zeolite, P-type zeolite and new products respectively. Starting materials with composition of $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O} = 5.0 : 1.0 : 3.9 : 160$ for NaX were heated at 90°C . The intermediate new products were prepared by the same composition. Because most of the synthetic zeolites are produced under non-equilibrium conditions and are considered, in a thermodynamic sense, as metastable phases. Upon the mixing of the reagents used in the synthesis, the system is in a disordered state with a which can exist in several different polymorphic forms, the one with the highest entropy will develop from the highly disordered synthesis mixture. According to the Ostwald rule of successive transformations, at long reaction times metastable zeolites recrystallize to other more stable structures under certain conditions.

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 synthesize most zeolite but complex in that there is little fundamental understanding of the processes operating during zeolite crystallization. This poor understanding of the complex crystallization process precludes predicting with any degree of certainty what method will successfully lead to large uniform crystals of NaX. It is our assessment that further experimental work is needed to establish the experimental conditions needed to produce the required zeolite product with a reproducible yield and crystal size distribution. and 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.

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 Y are obtained. The crystal of zeolite NaX is obtained in combined of octahedra (see Fig. 2). The crystal of NaX zeolite was obtained by measurements on an scanning electron microscopy of "diameters" of the $1\sim 3\mu\text{m}$ crystals observed in the final crystallization product after the different intervals of crystallization time from the start of heating. According to the increasing crystallization times, NaX zeolite was an increase in the upper size of $3\mu\text{m}$ and then new product was formed from the crystallization period of 3 to 9 days with same chemical composition of NaX zeolite ($5.0\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3.0\text{SiO}_2 \cdot 160\text{H}_2\text{O}$)(see Table 1). Fig. 2(a) shows the SEM images of the product at one day by hydrothermal reaction of zeolite NaX by amorphous SiO_2 seed. The product in an induction period for each zeolite appeared to be an agglomerate of NaX particles approximately $1\sim 1.5\mu\text{m}$ in size. A mixture of large crystals of zeolite NaX and NaP was observed in SEM images of intermediate reaction products, as show in Fig. 2(b), which is consistent with XRD evidence for the presence of crystalline zeolite NaP. Octahedral($11\mu\text{m}$) crystals were observed for well crystallized zeolite NaX (see Fig. 2(c)).

4. Conclusion

The addition of small amount of some seed elements (amorphous SiO_2 or NaX) significantly promotes the crystallization of zeolites, as compared to a synthesized zeolite by Zhdanov methode. The amorphous SiO_2 seed method not only accelerates the crystallization but also leads to a increase in size of crystals in the final crystallization product. but the modification form NaX zeolite crystal to new type zeolite is much too fast. NaX zeolite crystal of a particle size of about

8 μm ~11 μm are grown from Zhdanov method for 5 and 9 days in a mother liquor having an reactant composition $4.12\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3.5\text{SiO}_2 \cdot 593\text{H}_2\text{O}$. With increasing crystallization times, Na-P zeolite recrystallize to NaX zeolite

5. References

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Table 1 Crystal Size Growth of NaX Zeolite and Structure Types as function of Crystallization Time

sample No.	Digestion time(d)	Reactant Composition	structure Type	Crystal Size(μm)
X-B-1	1	$(5.0\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3.9\text{SiO}_2 \cdot 160\text{H}_2\text{O})$	X	1.0
X-B-3	3		$X \gg N$	1.5
X-B-6	6		$X > N$	2.5
X-B-9	9		$X \geq N$	3.0
X-S-1	1	$(5.0\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3.9\text{SiO}_2 \cdot 160\text{H}_2\text{O})$	X	1.0
X-S-3	3		X	3.0
X-S-6	6		N	-
X-S-9	9		N	-
X-X-1	1	$(5.0\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3.9\text{SiO}_2 \cdot 160\text{H}_2\text{O})$	X	1.0
X-X-3	3		$X \gg N$	-
X-X-6	6		$X > N$	2.7
X-X-9	9		N	-
X-Z-2	2	$(4.12\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3.5\text{SiO}_2 \cdot 593\text{H}_2\text{O})$	amorphous	-
X-Z-5	5		$P \gg X$	8
X-Z-9	9		$P > X$	11

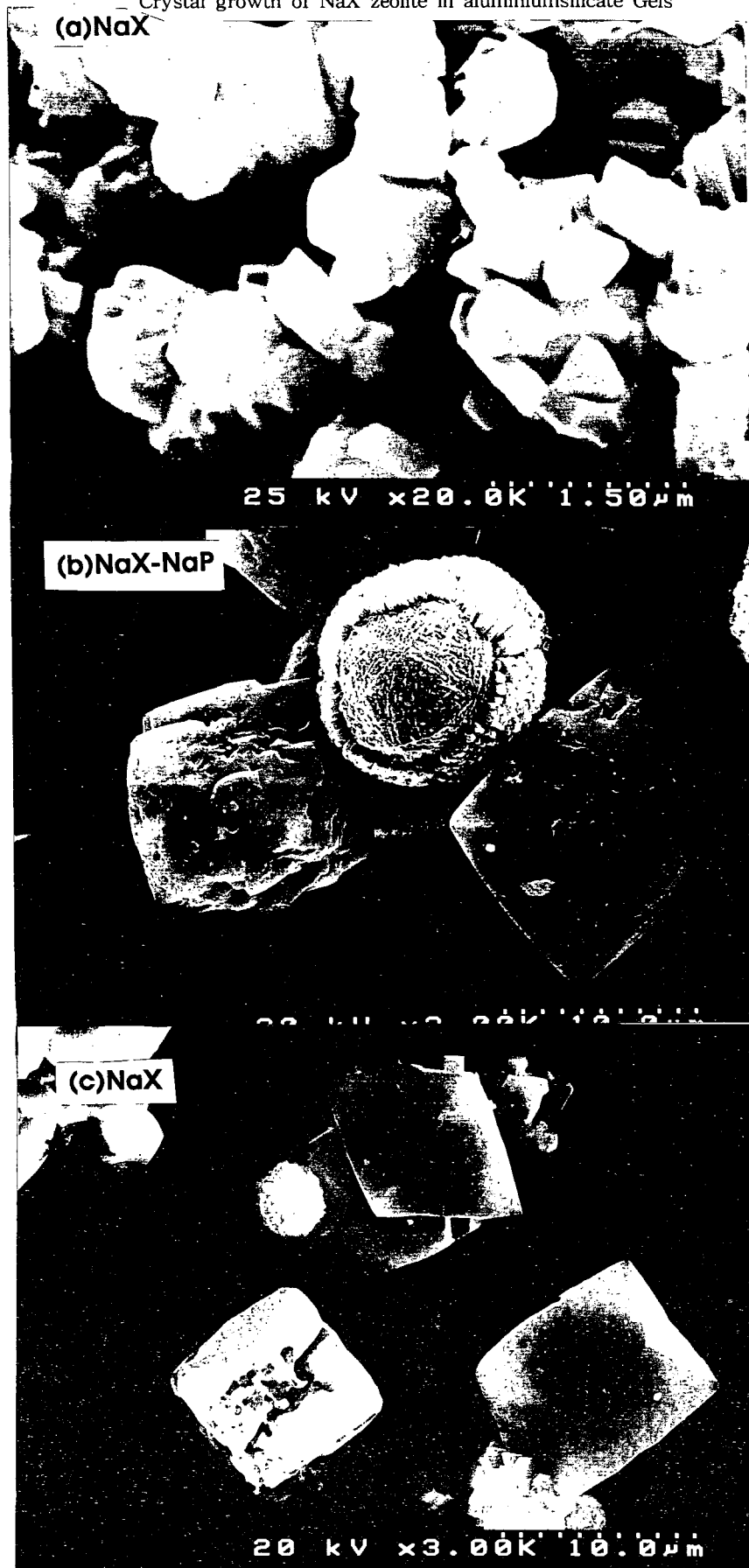


Fig. 2 SEM micrographs of (a)NaX, (b)NaX-NaP and (c)NaX Zeolite as function of crystallization times

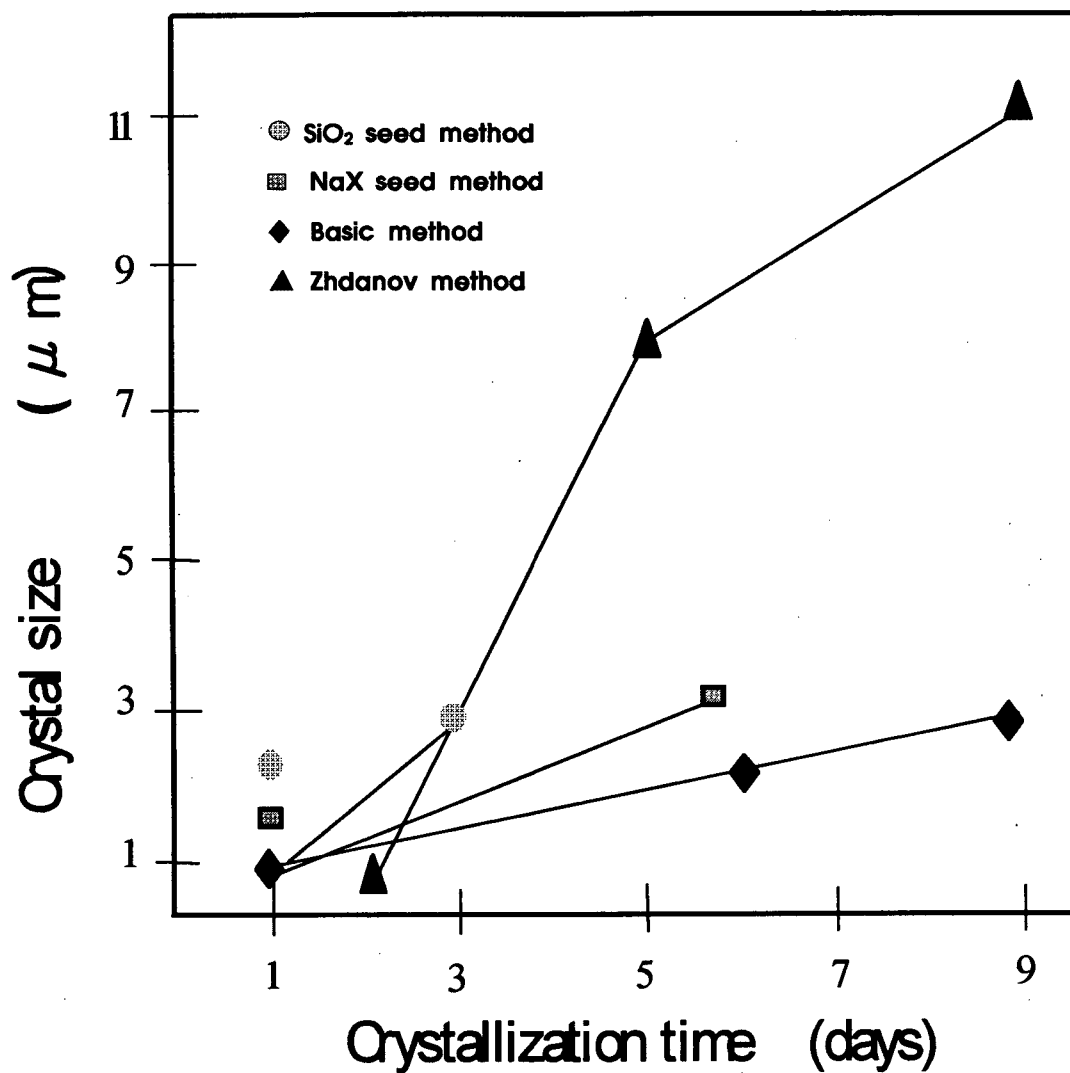


Fig. 3 Crystal size growth of NaX Zeolite as function of crystallization time