Crystal Growth of NaA, NaP and NaX Zeolite

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1. Introduction

Crystalline alumino silicate zeolites structurally consist basically of an open three-dimensional framework of SiO_4 and AlO_4 tetrahedra. Such tetrahedra are cross-linked by the sharing of oxygen atoms, so that the ratio of oxygen atoms to the total of aluminium and silicon atoms is equal to two. The negative electrovalence of tetrahedra containing aluminium is balanced by the inclusion within the crystal of cations, such as alkali or alkaline earth metal ions.

NaA and NaX Zeolite are of considerable industrial importance because of their catalytic, sorptive, and ion-exchange properties. Moreover, NaX crystals are used 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 to render the desiccant fit for re-use.

A method of preparing larger crystals of the zeolite NaA and 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 NaA and NaX zeolite under the influence of different experimental 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 $Na_2O : Al_2O_3 : SiO_2 : H_2O = 5.5 : 1.0 : 2.0 : 160$ for NaA, $Na_2O : Al_2O_3 : SiO_2 : H_2O = 5.0 : 1.0 : 3.0 : 160$ for NaX, and $Na_2O : Al_2O_3 : SiO_2 : H_2O = 4.0 : 1.0 : 4.0 : 160$ for NaP were prepared by hydrothermal treatment.

Schematic diagram of the preparation and crystal growth of Zeolite A and X is shown in Fig. 1. All of the required water for the bach 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 mixture was heated rapidly to 90℃. Sample of the heated mixture, crystallized at 90~95℃ for times raging from 1 hour to 15 days, were taken. Crystallized samples were allowed to cool and given the filtering, washing and drying treatment. Theses samples were analyzed for purity by X-ray and for crystal form and growing by SEM.

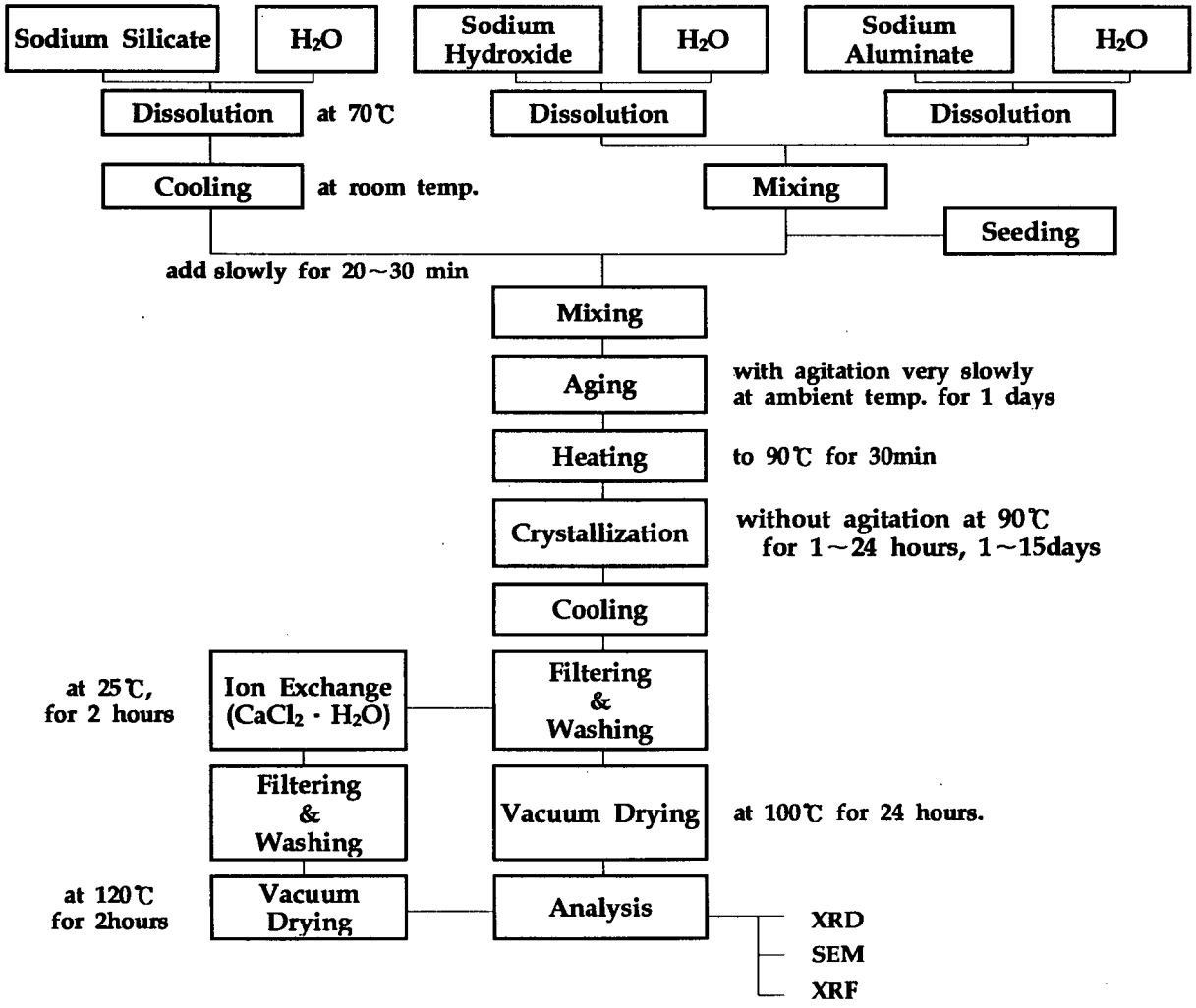

Fig. 1. Flow chart for zeolite synthesis.

3. Results and conclusions

We have investigated the effect of crystallization temperatures and how other phases such as zeolites A, X, and P can be formed from the same synthesis mixtures. We have also studied how both crystallization time and the presence of templates influence crystal size. XRD patterns were recorded on a MXP-18 system using CuKα radiation. Peak intensities were measured at given diffraction angles (2θ) : 7.30°, 6.16°, 12.5°, and 24.3° for NaA, NaX, NaP zeolite, and new products respectively. Starting materials with composition of $Na_2O : Al_2O_3 : SiO_2 : H_2O = 5.50 : 1.00 : 2.00 : 160$ for NaA and $Na_2O : Al_2O_3 : SiO_2 : H_2O = 5.0 : 1.0 : 3.9 : 160$ for NaX were heated at 363~368K. NaP zeolite and the intermediate new products were prepared by the starting material of $Na_2O : Al_2O_3 : SiO_2 : H_2O = 4.0 : 1.0 : 4.0 : 160$ for NaP and $Na_2O : Al_2O_3 : SiO_2 : H_2O = 5.0 : 1.0 : 2.5 : 160$ for new products.

The crystal of 4A and 5A zeolite is refer to as sodalite, a turncated cubo-octahedron of 1.5μm and 2.5μm, respectively, formed by SiO_4^{4-} and AlO_4^{5-} tetrahedra. When these sodalite units are joined by four-member rings, zeolite A is obtained and when joined by half of the six-member rings, zeolite X and Y are obtained. The crystal of zeolite X is obtained in combined of octahedra. With increasing aging times, NaX zeolite was an increase in the upper size of 3μm. NaP zeolite and new product was formed from the aging period of 3 to 5 days with same chemical composition of NaX zeolite ($5.0Na_2O \cdot Al_2O_3 \cdot 3.0SiO_2 \cdot 160H_2O$). NaP zeolite crystals size of 3μm are grown crystals of about 6 to 9μm from an aging period of 1 day to 6 and 14 days.

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 A, X, and P zeolite

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.

4. References

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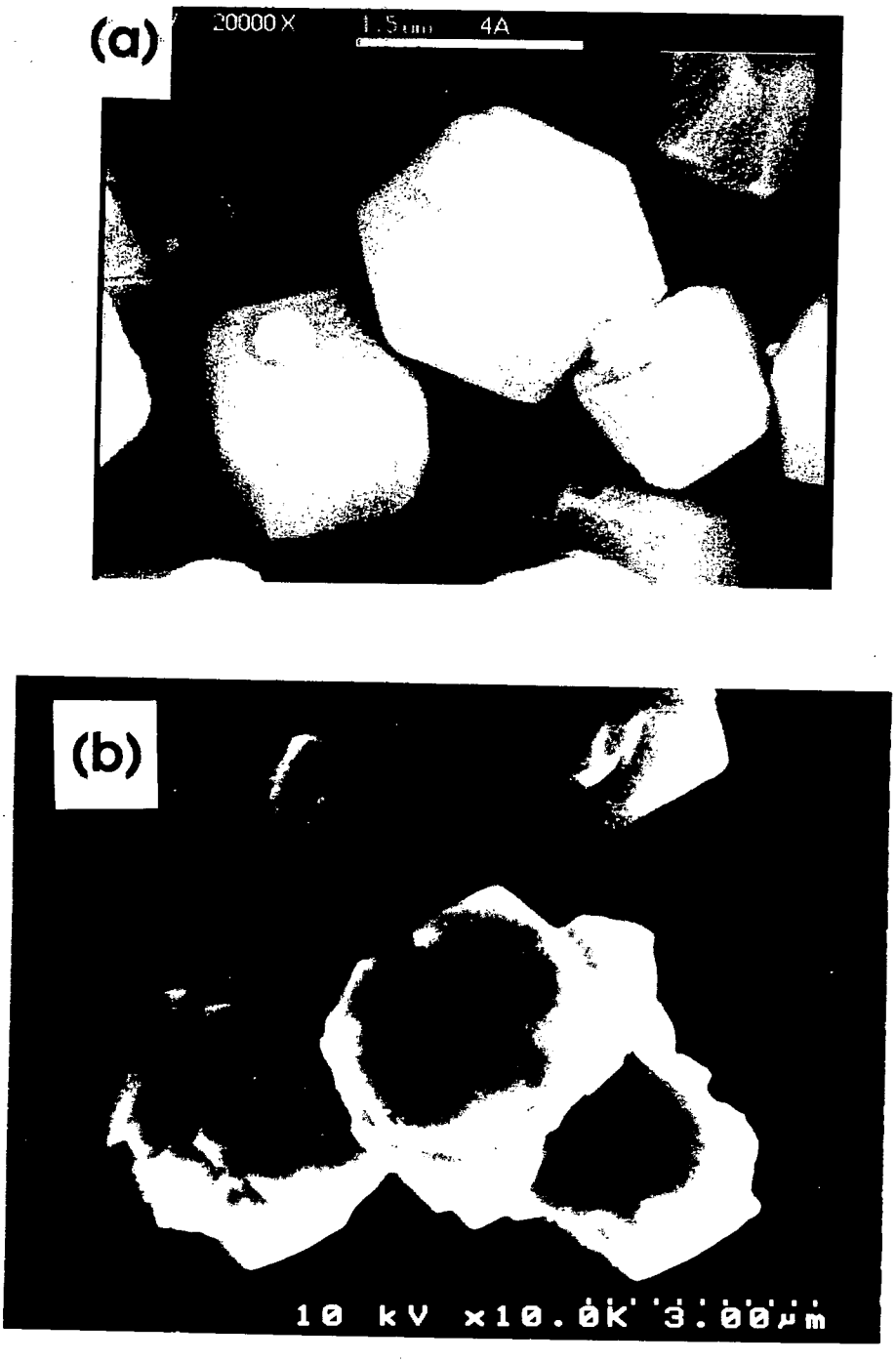

Fig. . SEM images of hydrothermal reaction products (a) NaA, (b) NaX.

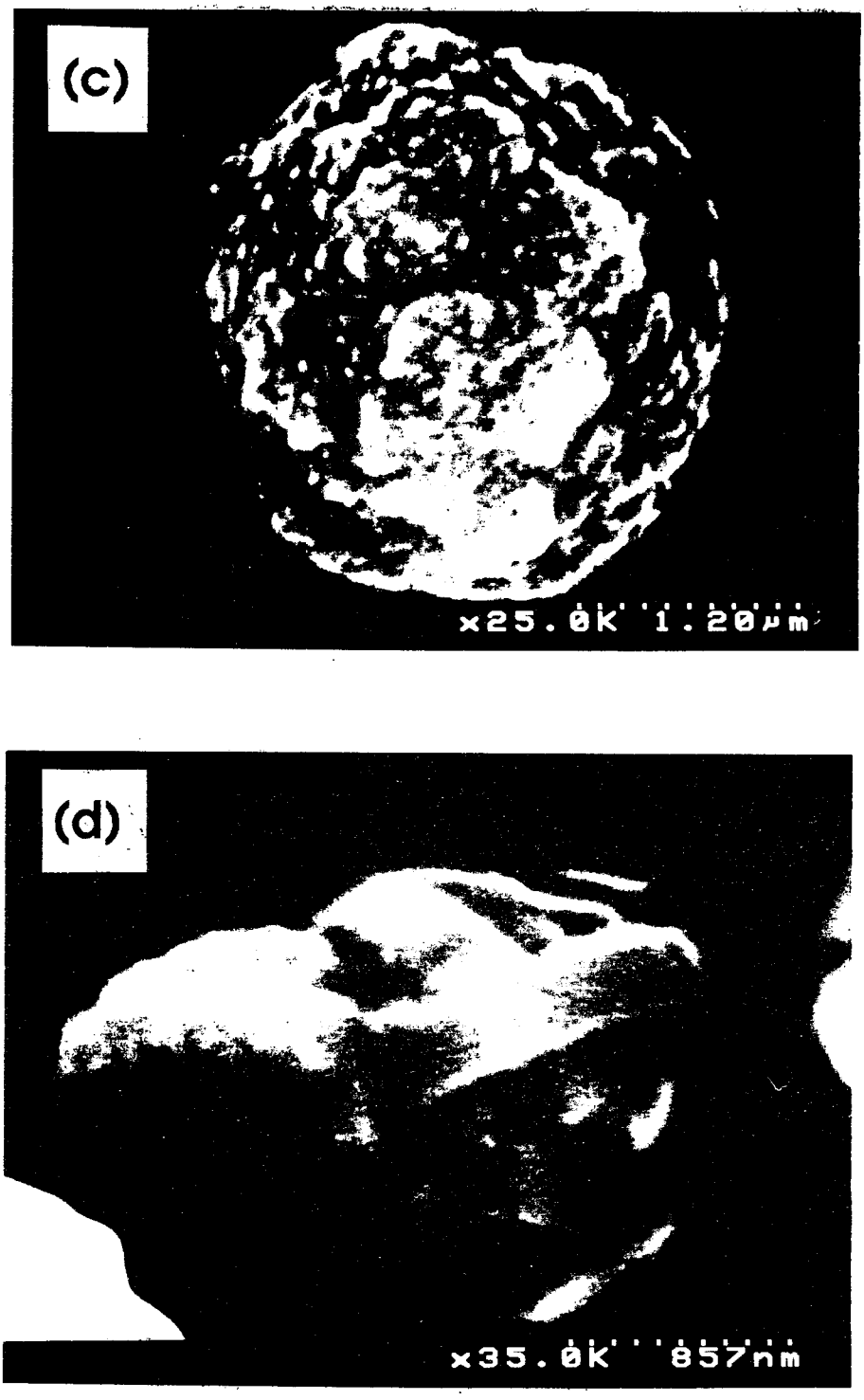

Fig. . SEM images of hydrothermal reaction products (c) NaP, (d) New product.

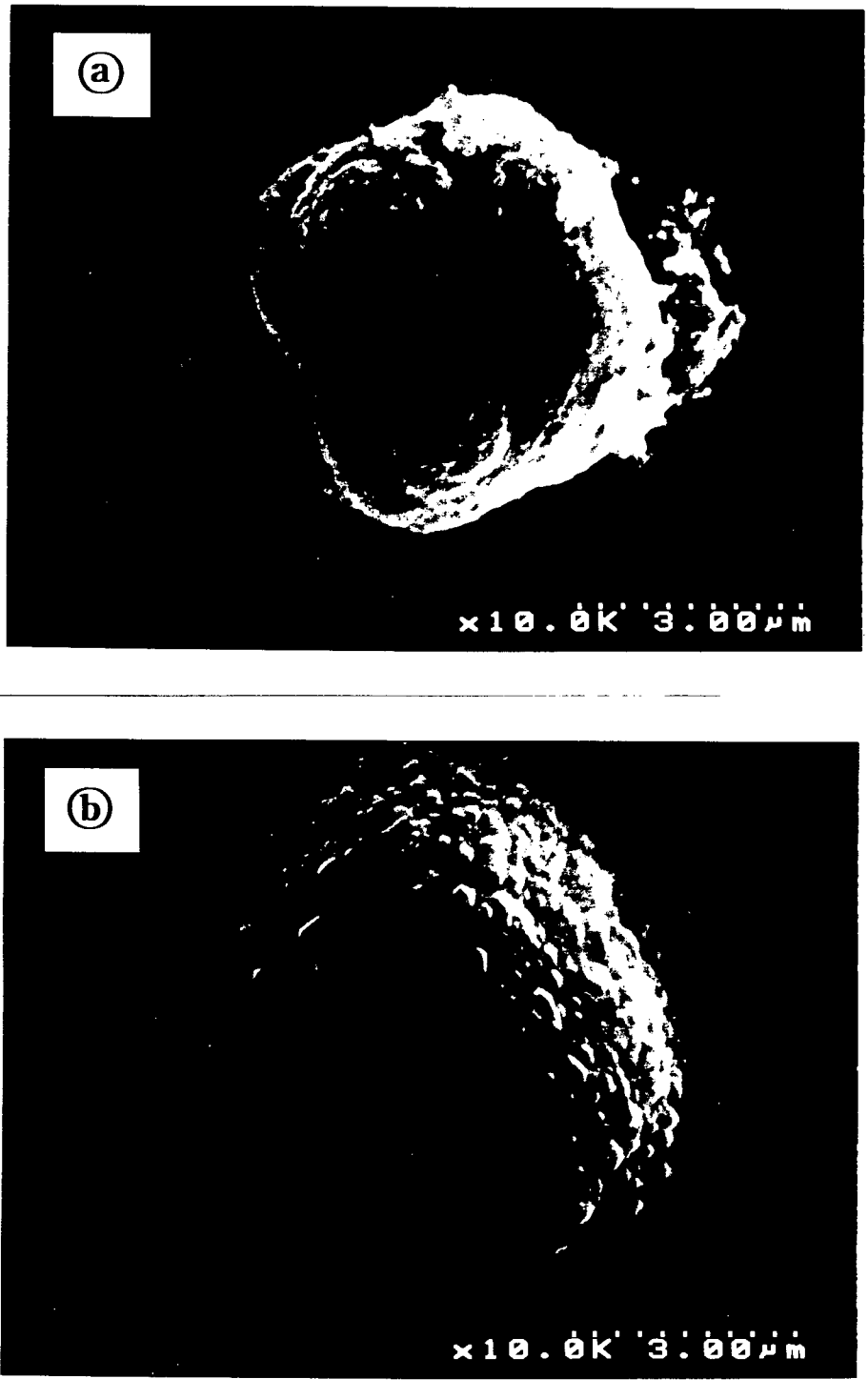

Fig. . SEM of the Synthesized Zeolite as a function of crystallization time at 90℃ by TEA method

ⓐ 1 day ⓑ 6 days ($Na_2O \cdot Al_2O_3 \cdot 2.8SiO_2 \cdot mH_2O \cdot 2.0TEA$)