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Step-like crystallization of BEA zeolite: Accumulation of oligomeric species in liquid phase followed by the conversion of solid phase to crystals

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In this study, the hydrothermal reactions of the synthesis mixtures of BEA zeolite and the synthesis cakes prepared by the filtration of the synthesis mixtures were investigated. The crystallization curves constructed based on the XRD patterns and the SEM images of the solid phases recovered at different reaction times exhibited step-like curves characterized by very long induction periods (70 h for the synthesis mixtures and 37 h for the synthesis cakes) and a short crystal growth time (4 h for both) at 150 °C. The higher concentration of the reactants in the synthesis cakes than in the synthesis mixture quickly generated more nuclei, consequently forming smaller crystals. In order to elucidate the changes occurring in the course of the hydrothermal reaction, a total of seven additional analysis techniques including ^{29}Si MAS NMR spectra, TEM, IR, and UV–Vis spectra were applied to the solid and liquid phases recovered at various times. No significant changes were observed in the solid phases during the induction period in terms of the crystallinity, chemical environment of silicon atoms, porous properties, capture state of structure-directing agent, and the IR bands of the hydroxyl groups, whereas the contents of oligomeric aluminosilicates increased in the liquid phases. Based on these analyses, the long induction periods were required for sufficient accumulation of the building blocks, and the blocks rapidly assembled to form BEA zeolite crystals in the subsequent growth stage, resulting in the step-like crystallization curves.

1. Introduction

Zeolites have been widely used as catalysts, adsorbents, and detergent builders in industries and households owing to their uniform pore entrances and shapes, adjustable acid-base properties, and high contents of exchangeable cations [1]. The steadily increasing demand for zeolites has driven investigation into cost-effective and eco-friendly synthesis methods [2]. Because the precise control of various zeolite properties in terms of crystallinity, shape, and Si/Al molar ratio is crucial to their performance [3–8], the understanding of their crystallization progress is an important research topic. Therefore, the changes occurring in the solid and liquid phases during the hydrothermal reaction have been intensively studied to obtain zeolite crystals with desired properties.

BEA zeolite is one of useful catalysts used in catalytic cracking [9], isomerization [10], and alkylation [11] processes in the petrochemical industry. It has relatively large pore entrances comprising 12 oxygen rings (12 MR), which allow large molecules to enter the pores and diffuse rapidly in its three-dimensional pore networks [11]. The wide range of Si/Al molar ratio (5–∞) of BEA zeolite also makes it possible to control its acidity in terms of the number and strength of acid sites [12,13]. The mild acidity and large pores of BEA zeolite are suitable for application as an effective catalyst for the preparation of 3,3-dimethyl-4,4-diaminodiphenylmethane [14]. In addition, the high hydrothermal stability of silica enriched BEA zeolite is also suitable for a regenerable adsorbent with a long service time for harmful pollutants emitted from diesel engines at cold start [15].

BEA zeolites have been conventionally synthesized by the hydrothermal reaction of synthesis mixtures comprised of silica and alumina sources, structure-directing agent (SDA), mineralizing agent, and water [1]. Various sources of silica and alumina can be

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used, whereas tetraethylammonium hydroxide (TEAOH) has been predominantly used as the SDA. The compositions such as SiO_2/Al_2O_3, TEA_2O/SiO_2, and H_2O/SiO_2 of the synthesis mixtures largely affect the crystallization rate of BEA zeolite [3,16–18]. For example, BEA zeolite is rapidly crystallized in a synthesis mixture with the SiO_2/Al_2O_3 and TEA_2O/SiO_2 ratios of 100 and 0.27, respectively, because of its short induction period and high crystal growth rate. The increase in the TEA_2O/SiO_2 ratio leads to a longer induction period and a slower crystal growth rate.

Although the hydrothermal reaction of the synthesis mixtures can be easily carried out in a simple reactor to prepare BEA zeolite, it also has several disadvantages. The small contents of silica and alumina sources in the synthesis mixtures lower the production yield of BEA zeolite, and the large reactor volume and huge energy consumption considerably increase the production cost [2,19,20]. In addition, the relatively long reaction time for its crystallization is a typical demerit [3–5,16]. The dry gel conversion method significantly shortens the reaction time, but the complicated preparation steps of reactants are disadvantageous in commercial manufacturing process. A solvent-free synthesis facilitates the preparation of BEA zeolite with a small reactor and reduces energy consumption, but impurities in products and heterogeneous particle sizes hinder its commercial applications [2].

The hydrothermal reaction of the synthesis mixtures of BEA zeolites in a batch reactor usually exhibits an S-type crystallization curve, because of the autocatalytic growth of zeolite crystals and the limited amounts of source materials [21]. Although the shape of the crystallization curve varies with the mixture composition and the reaction temperature, a step-like curve with an extraordinarily long induction period and a relatively short crystal growth time was observed in the hydrothermal reaction of BEA zeolite under particular reaction compositions [2,17]. The long induction period is related to an abnormally slow nucleation rate, which is subsequently attributed to the difficulty in the formation of nuclei from ionic species. In such case, one might presume that some important reactions should occur during the induction period to form some species functioning as building blocks, and consequently the observed relatively rapid crystal growth following the induction period indicates crystallization reactions between the pre-formed species, not between the ionic species. Several papers reported the step-like crystallization curves in the preparation of BEA zeolite, but any clear interpretation has not been reported [3,18,22,23].

The synthesis of zeolite A from the synthesis cakes prepared by filtering its synthesis mixtures considerably reduces the reactor volume and energy required for the hydrothermal reaction [24]. Furthermore, the highly concentrated reactants in the synthesis cakes facilitate the rapid nucleation, reducing the reaction time and improving the uniformity of zeolite particle sizes. Taking these advantages, in this study, we examined the synthesis of BEA zeolite from its synthesis cakes to deduce a reasonable explanation for the changes occurring in the long induction periods and short crystal growth times. The liquid phases as well as the solid phases recovered in the crystallization of the synthesis cake at different reaction times were investigated using various analysis techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), ^{29}Si solid magic angle spinning solid (MAS) NMR, ^{29}Si liquid NMR, ultraviolet and visible (UV–Vis) spectrophotometry, infrared (IR) spectroscopy, and thermogravimetric (TG) analysis. The experimental results showed that extremely long induction period was required to accumulate the oligomeric species formed from silica and alumina species in the liquid phase. Furthermore, no appreciable change was observed in the solid phase during the induction period, and the subsequent rapid crystal growth resulted from the assembly of the accumulated building blocks of BEA zeolite.

2. Experimental

2.1. Synthesis of BEA zeolite

Sodium aluminate (39% Na_2O, 56% Al_2O_3, Junsei), colloidal silica (40% SiO_2, HS-40, LUDOX®, Sigma–Aldrich), sodium hydroxide (97%, Daejung), and TEAOH (40%, Sigma–Aldrich) were used as the reactants without further purification. The synthesis mixture with the composition of 25 SiO_2: 0.2 Al_2O_3: 3.0 Na_2O: 4.5 TEA_2O: 440 H_2O was stirred for 6 h to prepare a homogeneous mixture. The synthesis cake was prepared by filtering the synthesis mixture with a filter paper (Whatman No. 6, pore diameter; 3 μm) under reduced pressure. The synthesis mixture, synthesis cake, and filtrate were named BEA_SM, BEA_SC, and BEA_FL, respectively.

In order to examine the effects of the compositions of silica and alumina and the water content on the crystallization rate, we prepared two more synthesis cakes (BEA_SC2 and BEA_SC3) with different water contents by adding water to the original synthesis cake (BEA_SC). With reference to the composition 12.3 SiO_2: 0.17 Al_2O_3: 1.4 Na_2O: 3.9 TEA_2O: x H_2O of the synthesis cakes, the coefficient x increased from 115 for BEA_SC to 300 and 440 for BEA_SC2 and BEA_SC3, respectively. In addition, we prepared two more synthesis mixtures (BEA_SM2 and BEA_SM3) with less water contents than the original mixture (BEA_SM) by centrifuging. With reference to the composition 25 SiO_2: 0.2 Al_2O_3: 3.0 Na_2O: 4.5 TEA_2O: y H_2O of the synthesis cakes, the coefficient y decreased from 440 for BEA_SM to 300 and 200 for BEA_SM2 and BEA_SM3, respectively. The actual compositions of BEA_SM2 and BEA_SM3 were 20.4 SiO_2: 0.19 Al_2O_3: 2.4 Na_2O: 4.2 TEA_2O: 320 H_2O and 15.7 SiO_2: 0.18 Al_2O_3: 1.9 Na_2O: 4.1 TEA_2O: 200 H_2O, respectively.

The hydrothermal reactions of BEA_SM and BEA_SC were carried out in Teflon autoclaves (Parr Instrument) equipped with 20 mL Teflon vessels. The autoclaves were charged with the synthesis mixtures and cakes and put in an oven controlled in the temperature range 140–160 °C for specified reaction times. The autoclave was pulled out and rapidly cooled with tap water. The solid phases were recovered by centrifuging, washed with deionized water, and dried in an oven of 90 °C overnight. They were calcined at 550 °C for 4 h to remove the occluded TEA_2O. The pH of reactant was measured using a pH meter (pH-220L, ISTEK Inc.).

2.2. Characterization of BEA zeolite

The XRD patterns of the solid phases recovered during the hydrothermal reaction of BEA_SM and BEA_SC were recorded using a high-resolution X-ray diffractometer (HR–XRD, Xpert pro multipurpose high-resolution X-ray diffractometer, PANalytical). Cu Kα X-ray radiation ($\lambda = 1.54056$ Å) was used for scanning in the 2θ range 5–40° under the operating conditions of 60 kV at 55 mA. The shape and size of the solid phases were examined by field-emission SEM (FE-SEM, S-4700, Hitachi), and their compositions were determined by an energy dispersive X-ray spectrometer (EDX, EX-200, Horiba) attached to the FE-SEM. The compositions of silica and alumina were also confirmed using an electron probe micro analyzer (EPMA, EPMA-1600, Shimadzu). ^{29}Si solid MAS NMR spectra of the solid phases in the range −70 to −130 ppm were recorded using a NMR spectrometer (Unity Solid Inova WB 200 MHz system, Varian). The pulse size of 39.7 MHz radiation was 6.0 μs, with a delay time of 10 s. ^{29}Si NMR spectra of the liquid phases were obtained using another NMR spectrometer (Liquid NMR, ProPulse 500 MHz NMR spectrometer, Agilent). Deuterated water (D_2O, 99.9% D, Sigma–Aldrich, 1 mL) was added to the liquid phases before recording their NMR spectra. After diluting the liquid phases with deionized water, their UV–Vis spectra were recorded using a UV–Vis spectrophotometer (Mini-D2, Ocean Optics Inc.).