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Fine control of particle size by seeding and ageing under agitation in the synthesis of analcime zeolite

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Abstract−The size of analcime particles produced through hydrothermal reactions of alkaline synthesis mixtures was finely controlled by seeding and ageing under agitation. Adding acid-treated analcime seeds to the synthesis mixture followed by ageing in an agitated vessel facilitated further nucleation, which resulted in the formation of fine analcime particles with an extremely narrow size distribution. The size of analcime particles could be controlled in the range of 0.5-5.0 μm with a standard deviation of less than 0.1 μm by varying the amount and type of the acid-treated seeds, the ageing time, and the agitation speed.

Keywords: Analcime, Particle Size, Seeding, Ageing, Agitation

INTRODUCTION

Zeolites have been synthesized through hydrothermal reactions of synthesis mixtures containing silica and alumina sources along with alkaline species and structure directing agents [1-4]. The mixture composition and the reaction conditions primarily determine the type of zeolite frameworks [5,6] and the shape and size of zeolite particles [7-17]. The application of zeolites as catalysts, adsorbents, or detergent builders is usually determined by the size and shape of their pore structures, which restricts the entrance of reactants and adsorbates, but their performance is also affected by the particle sizes. The shape-selective catalysis of a ZSM-5 zeolite observed in the alkylation of toluene with methanol becomes more effective with a larger particle size [18]. On the contrary, a smaller SAPO-34 catalyst particle exhibits better performance in methanol-to-olefin conversion due to the more numerous pores accessible by methanol and the shorter path for the diffusion out of the produced olefins [19]. Zeolite A used as a detergent builder shows the best performance in terms of cation exchange rate and handling convenience when its particle size is finely controlled in the range of 1-2 μm [16]. As these examples illustrate, the control of particle size in zeolite synthesis has received growing interest.

Since zeolite particles usually grow from nuclei during hydrothermal reactions, the concentration of nuclei in the synthesis mixtures is very important for the final particle sizes. Since the source materials are limited in a batch reactor, a higher concentration of nuclei results in smaller zeolite particles [15,20]. Although the growth of zeolite particles definitely occurs on the nuclei, the actual state of the nuclei and their generation mechanism have remained controversial.

A well-known method to obtain uniformly sized zeolite particles is the addition to the synthesis mixtures of seeds that act as nuclei in the crystallization of zeolites [21-23]. The primary purpose of seeding is to produce only a certain type of zeolite, but the consequent increase of nuclei reduces the crystallization time and thus enhances the productivity of zeolites. In our previous study, we used large acid-treated analcime (ANA) particles as seeds for the synthesis of analcimes of different particle sizes with very narrow distributions [23]. Since the acid treatment of analcime selectively eliminates alumina from its framework, a large analcime particle is divided into many small analcime moieties with its apparent shape retained. While low concentration acids produce many thin cracks that divide the analcime particle into many small zones, high concentration acids remove excessive aluminum to leave a small number of cracked pieces.

Ageing of the seeded synthesis mixture under agitation is expected to produce more nuclei than those obtained from the immediate hydrothermal reaction of the seeded mixture. The acid treatment carried out in the preparation of the analcime seeds rendered the particles so fragile that they could be easily shattered into pieces in the shear field aroused by agitation. The shattered pieces are expected to serve as the nuclei on which analcime crystals grow in the subsequent hydrothermal reaction.

We report here a new method that combines seeding and ageing under agitation to synthesize small, uniformly sized and pure analcime particles. The outcome of the scheme will be compared with those obtained both from an unseeded synthesis mixture and from seeded but unaged mixtures in terms of particle sizes and distributions. The new method is expected to provide an effective way of finely controlling the particle size in the synthesis of analcime.

EXPERIMENTAL SECTION

1. Synthesis of Analcime from the Synthesis Mixtures Containing Seeds

Large analcime particles with an average diameter of 25 μm to

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be used as seeds were prepared from alkaline silicate and aluminate solutions, as described in our previous paper [23]. The analcime was treated with hydrochloric acids of various concentrations under reflux at 90 °C for 2 h before use. The acid treatment caused cracks on the surface of the analcime particles, but stronger acids made the particles break into a few pieces, as shown in Fig. S1 (see Supplementary Information). The prepared seeds were named 'ANA_Ax', with 'x' denoting the normal concentration of acid used in the treatment. The amount of seeds added to the synthesis mixture was denoted as a weight percentage of the mixture.

Analcime particles with exceptionally narrow size distribution were synthesized by adding ANA_Ax seeds to a synthesis mixture comprising 25.0 Na_2O : 1.0 Al_2O_3 : 11.5 SiO_2 : 840 H_2O moles. Sodium silicate (Daejung, 30 wt% SiO_2), sodium aluminate (Junsei, 56 wt%, Al_2O_3), and sodium hydroxide (Daejung, 98 wt%) were used in the preparation of the synthesis mixtures. Since the sodium hydroxide content of the synthesis mixtures was considerably higher than that used in the synthesis of analcime reported in the literature [4], sodalite (SOD), which is denser than analcime, was expected to be produced together. The seeded synthesis mixtures were aged at varying agitation rates for different times in a circulator maintained at 5 °C, which is cool enough to suppress the growth of zeolite particles. A magnetic stirrer was operated at 200, 300, and 500 rpm for agitation. All the synthesis mixtures were crystallized to analcime at 170 °C for 3 h in an oven rotating at 100 rpm. After the reaction, the zeolite products were centrifuged, washed several times with deionized water and ethanol, and sonicated before drying at 100 °C in an oven.

2. Characterization

The crystal structures of analcime and crystallizing gel were investigated by a high-resolution X-ray diffractometer (XRD; PANalytical, X'Pert PRO Multi Purpose). The particle size distribution of the produced zeolites was obtained by using a scanning electron microscope (SEM; JEOL, JSM-7500F) and a particle size analyzer (PSA; Otsuka Electronics, ELS-8000). The SEM was used to examine the shape and size of the analcime particles. Despite the uniform size and shape of the analcime particles produced, the diameters of more than 100 particles were measured for improved precision. The PSA, equipped with a photon-counting photomultiplier detector and a 10 mW He-Ne Laser, was used to measure the particle

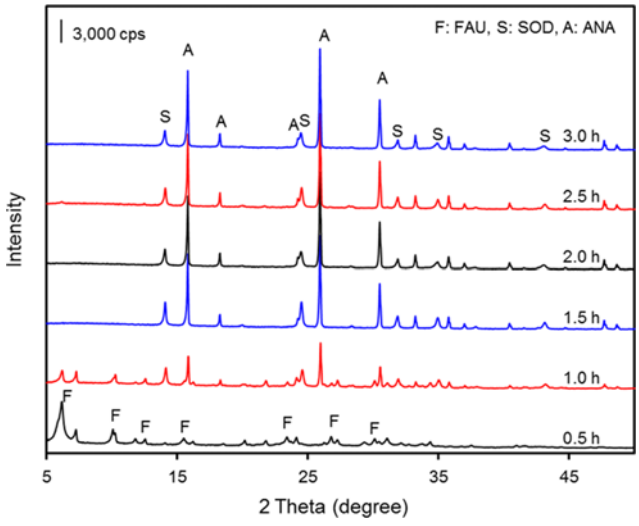


Fig. 1. XRD patterns of products obtained in hydrothermal reaction of the synthesis mixture at 170 °C.

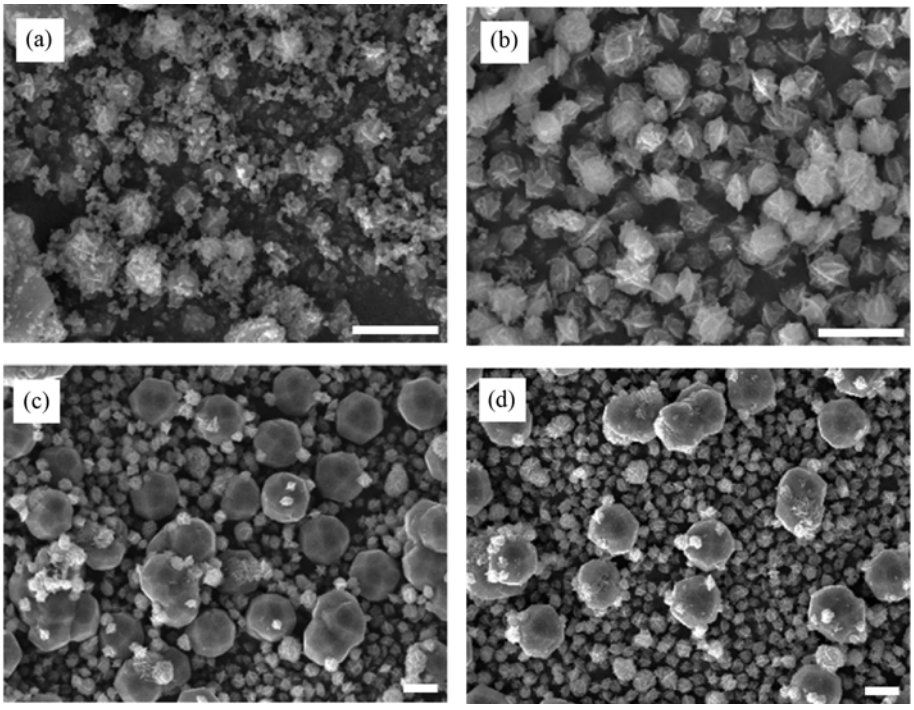


Fig. 2. SEM photos of products obtained in hydrothermal reaction of the synthesis mixture without seeding for different times at 170 °C: (a) for 1 h, (b) for 1.5 h, (c) for 2 h, and (d) for 3 h. The inserted scale bars represent 5 μm.

size distribution of the analcime particles.

RESULTS AND DISCUSSION

In a synthesis mixture without seeds, nucleation under supersaturation followed by crystal growth results in the production of zeolite particles [15]. Fig. 1 shows the XRD patterns of products obtained through the hydrothermal reaction of the synthesis mixture aged for 1 d. Seven XRD peaks were observed at 2θ=6.1°, 10.0°, 11.7°, 15.4°, 23.3°, 26.7°, and 31.0° from the solid phase obtained after 0.5 h reaction. These peaks were attributed to faujasite (FAU), but their small sizes indicated the low faujasite content [24]. With increasing reaction time, several XRD peaks showed rapid increases: the peaks at 2θ=14.2°, 24.7°, 32.0°, 35.1°, and 43.4° were responsible for sodalite and those at 2θ=15.8°, 18.3°, 24.3°, 26.0°, and 30.5° for analcime [24]. The simultaneous growth of these peaks represented the co-production of analcime and sodalite accompanied by a decrease in faujasite content. The relatively rapid growth of the analcime peaks compared with the sodalite peaks suggests that analcime formation was preferred under the reaction conditions. The simultaneous formation of analcime and sodalite could be confirmed again from the SEM photos shown in Fig. 2. The solid phases obtained after 1 h and 1.5 h did not show any definite shape responsible for either analcime or sodalite. However, the particles of 4.6-5.9 μm in diameter with definite facets observed from the solid phases obtained after 2 h and 3 h were analcime, while the small particles of 1.6-1.7 μm with a flower-like shape were sodalite. These matches between the shapes and the zeolite types were provided by our previous work [23].

Since the zeolites crystallize on the surface of the zeolite nuclei and particles, the presence of seeds in synthesis mixtures largely influences the shape, size and type of the synthesized zeolites. This

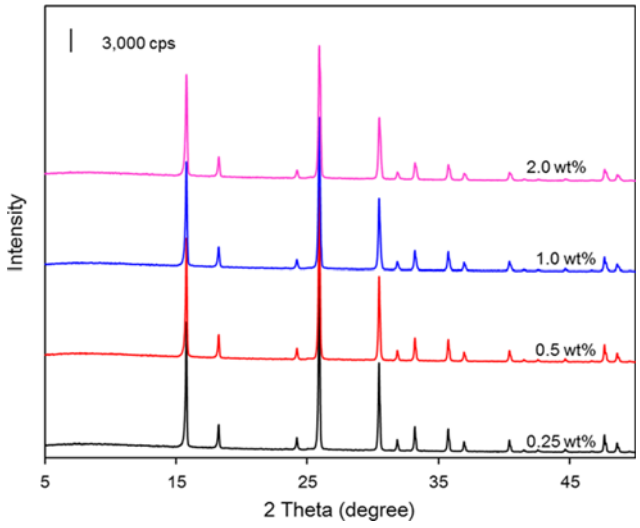


Fig. 3. XRD patterns of analcimes synthesized from the synthesis mixtures containing different amounts of ANA_A2.0 seeds at 170 °C for 3 h.

seeding effect can be clearly seen in Fig. 3, which shows the XRD patterns of solid phases obtained from the synthesis mixtures with different amounts of ANA_A2.0 seeds. The solid phases only exhibited XRD peaks attributed to analcime, indicating that the seeds added into the synthesis mixture determined the framework of the synthesized zeolites.

The products from the synthesis mixtures with different amounts of ANA_A2.0 seeds were well-faceted analcime particles, as shown in Fig. 4. A small amount of sodalite particles adhered on large analcime particles when the amount of the seed was as small as 0.25 wt%, but only analcime particles were observed when the amount

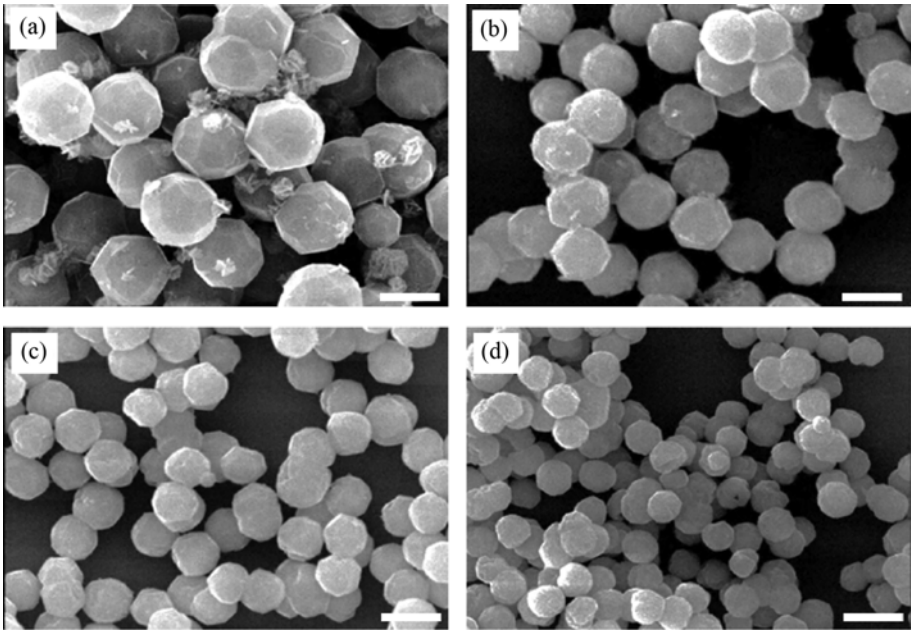


Fig. 4. SEM photos of analcimes synthesized from the synthesis mixtures containing different amounts of ANA_A2.0 seeds at 170 °C for 3 h: (a) 0.25 wt%, (b) 0.5 wt%, (c) 1.0 wt%, and (d) 2.0 wt%. The inserted scale bars represent 3 μm.

of the seed was larger than 0.5 wt%. In sufficient amount, the analcime seeds rapidly grew into analcime particles at high temperatures, excluding the possibility for the formation of sodalite nuclei in the synthesis mixture. The analcime particles thus obtained were pure and quite uniformly sized, and their average size gradually decreased as more seeds were added. This indicates that the analcime particles were only grown from the supplied seeds until the silica and alumina sources in the synthesis mixtures were exhausted.

Fig. S2 (see Supplementary Information) exhibits an SEM photo of analcime particles obtained from the synthesis mixture with 1.0 wt% ANA_A2.0 seeds, and compares the size distributions of the synthesized analcime particles determined on the basis of the SEM and PSA measurements. The produced particles were very uniform with an average particle size of 0.59±0.04 μm, as determined from the SEM photo, or either 0.50 or 0.60 μm, as determined from two PSA measurements. The poor match between the two PSA values might be due to the aggregation of small analcime particles induced by the high concentration of hydroxyl groups on the particles. Therefore, in this study, the average sizes of analcime particles were determined from the SEM photos. A similar attempt to determine the average size of zeolite particles from SEM photos has been reported [25], and it might be better to deduce the number of nuclei when the particle size distributions are sufficiently narrow.

The amount of analcime seeds in a synthesis mixture, in principle, determines the average size of analcime particles produced

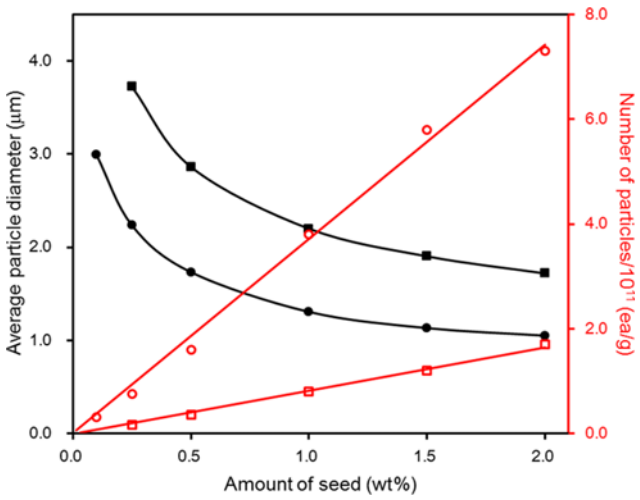


Fig. 5. Variations of the average diameter and number of analcime particles with the amount of seeds in the synthesis of analcime without ageing at 170 °C for 3 h. The seeds used are ANA_A1.0 (●, ○) and ANA_A2.0 (■, □).

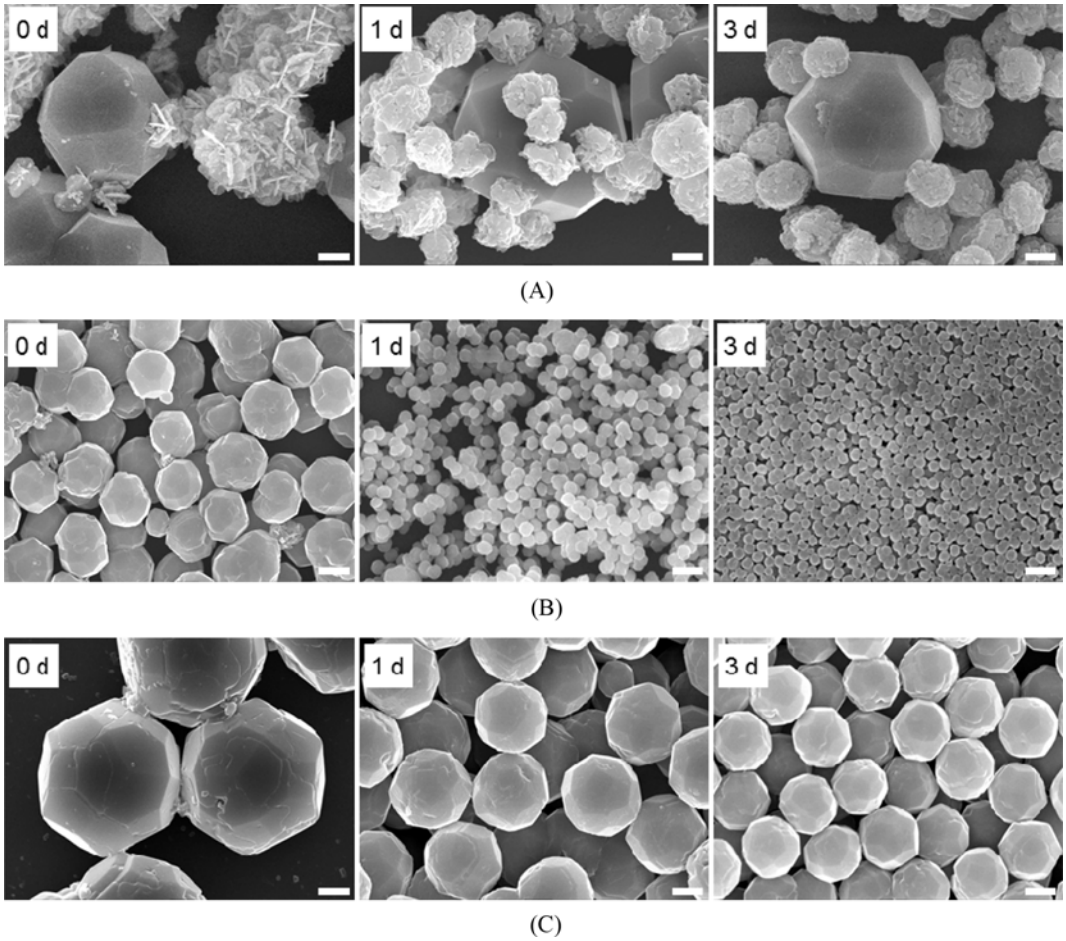


Fig. 6. SEM photos of analcime particles obtained from synthesis mixtures: (A) without seed, (B) with ANA_A1.0 seed, and (C) with ANA_A4.0 seeds. The synthesis mixtures were aged at 300 rpm for different ageing times. The inserted scale bars represent 1 μm.

when no further nucleation occurs during the hydrothermal reaction. Fig. 5 shows the variations of the size and number of analcime particles with the amount of seed in the crystallization of analcime. The linear relationships between the amount of seeds and the number of analcime particles produced from ANA_A1.0 and ANA_A2.0 confirmed that the particles only grew from the seeds. The average particle diameter gradually decreased with increasing seed amount, but did not reveal a linear relationship due to the difference between the dimensions of diameter and volume. The number of seeds in ANA_A1.0 and ANA_A2.0 was estimated from the linear slopes to be 3.8×10^{11} and 0.8×10^{11} per g seed, respectively. The fewer seeds in ANA_A2.0 confirmed that the higher acid concentration removed more aluminum in the zeolite framework and thus left fewer zeolite moieties in the seed [23]. Since crystallization was at the high temperature of 170 °C, the consumption of source materials was rapid enough to suppress further nucleation, resulting in the synthesis of analcime particles with a very narrow size distribution.

The ageing of the seeded synthesis mixtures under agitation for a given period significantly reduced the size of the synthesized analcime particles. Fig. 6 compares the SEM photos of analcime particles produced from an unseeded synthesis mixture with those from the mixtures seeded with ANA_A1.0 and ANA_A4.0. The particles from the unseeded mixture showed little variation in the species and size of zeolites regardless of the ageing time ranging from 0 to 3 d: both analcime and sodalite were obtained, as already observed in Fig. 2(d). However, only the uniformly sized analcime particles were synthesized from both the seeded mixtures, and their sizes consistently decreased with increasing ageing time.

The quantitative relationship between the particle sizes and the ageing time in the crystallization of the seeded synthesis mixtures is examined in more detail in Fig. 7. The standard deviation of the particle sizes was very small, and hence not shown for clarity. Regardless of the seed type, the average particle diameters showed monotone decreases with increasing ageing time: initially fast but gradually slower later. The average diameter of the analcime particles obtained from the synthesis mixture seeded with ANA_A4.0 decreased from 5.1±0.06 μm without ageing to 1.9±0.05 μm after ageing for 5 d.

The decrease in the average particle size of analcime indeed reflects the increase in the nuclei concentration of the seeded synthesis mixtures during the ageing under agitation. Although this increase of nuclei could be attributed to so-called secondary nucleation, it does not exactly match any of the three secondary nucleation mechanisms postulated in the literature: initial breeding, micro-attrition, and fluid-shear-induced nucleation [20]. Nevertheless, the increase of nuclei was certainly the result of the acid treatment-induced disintegration of the seed particles, which had been rendered fragile by the numerous internal cracks.

It seems evident that agitation is necessary to shatter a fragile seed particle into pieces in the synthesis mixture during ageing. This was confirmed by the SEM photos in Fig. S3 (see Supplementary Information), which show the analcime particles obtained from the synthesized mixtures seeded with ANA_A2.0 and ANA_A3.0, but aged in a stagnant vessel without agitation: the type of acid-treated seeds affected the sizes of the synthesized particles as expected, but the ageing time did not. Irrespective of ageing time, further nucleation did not occur without agitation. This observation is supported by Fig. 8, which shows the variation of the average particle diameter of analcime with ageing time. When the synthesis mixtures containing ANA_A1.0, ANA_A2.0, and ANA_A3.0 seeds were aged in a stagnant vessel, the particle sizes did not change, regardless of the ageing time. On the contrary, the particles crystallized from the synthesis mixture seeded with ANA_A4.0 exhibited a seemingly random variation, probably because the most fragile seed particles among the four were most susceptible to irregular breakage during the hydrothermal reaction.

Fig. 9 shows the effect of agitation speed on the analcime particle size during ageing of the synthesis mixtures. The SEM photos

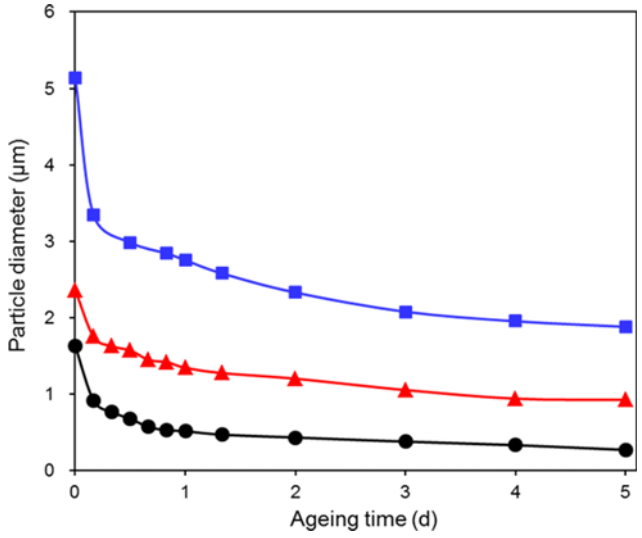


Fig. 7. Variation of the average diameter of analcime particles with ageing time from seeded synthesis mixtures under 300 rpm agitation at 170 °C for 3 h. The seeds used are ANA_A1.0 (●), ANA_A3.0 (▲), and ANA_A4.0 (■).

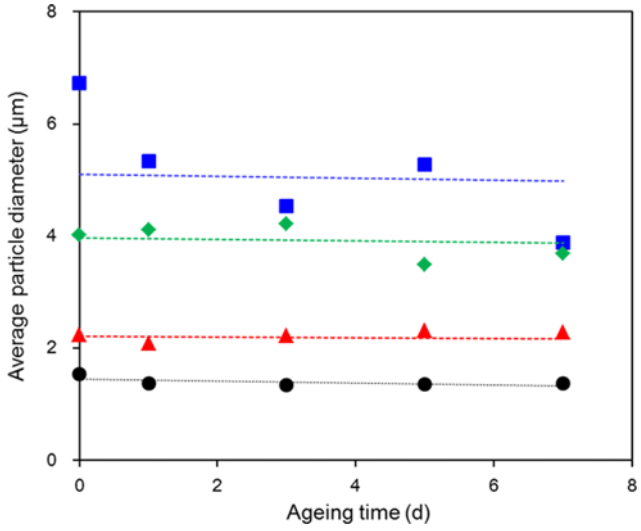


Fig. 8. Variation of the average diameter of analcime particles with ageing times from seeded synthesis mixtures without agitation at 170 °C for 3 h. The seeds used are ANA_A1.0 (●), ANA_A2.0 (▲), ANA_A3.0 (◆) and ANA_A4.0 (■).

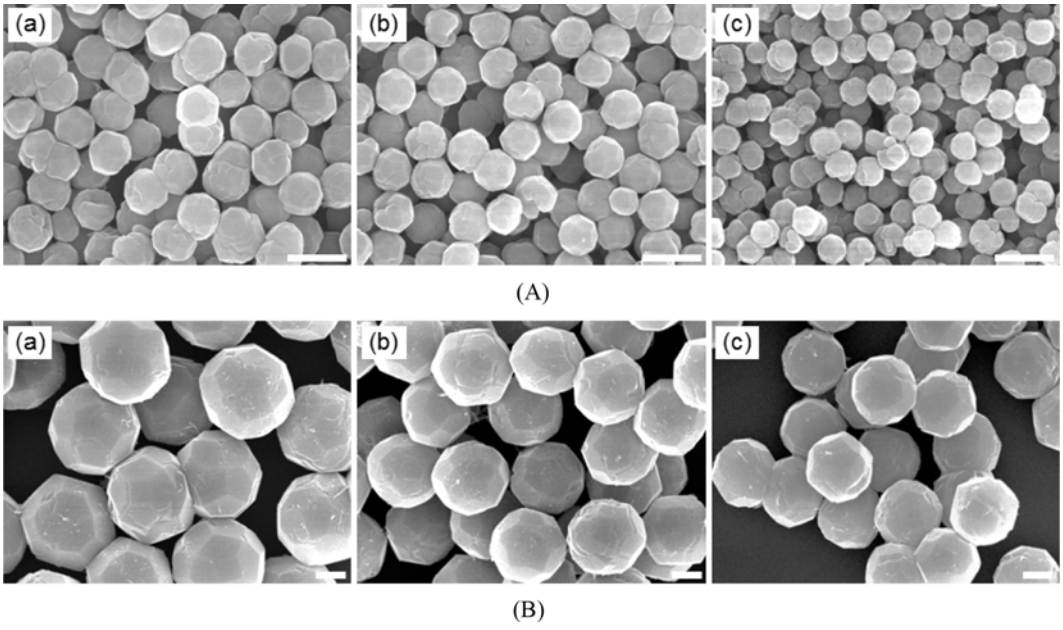


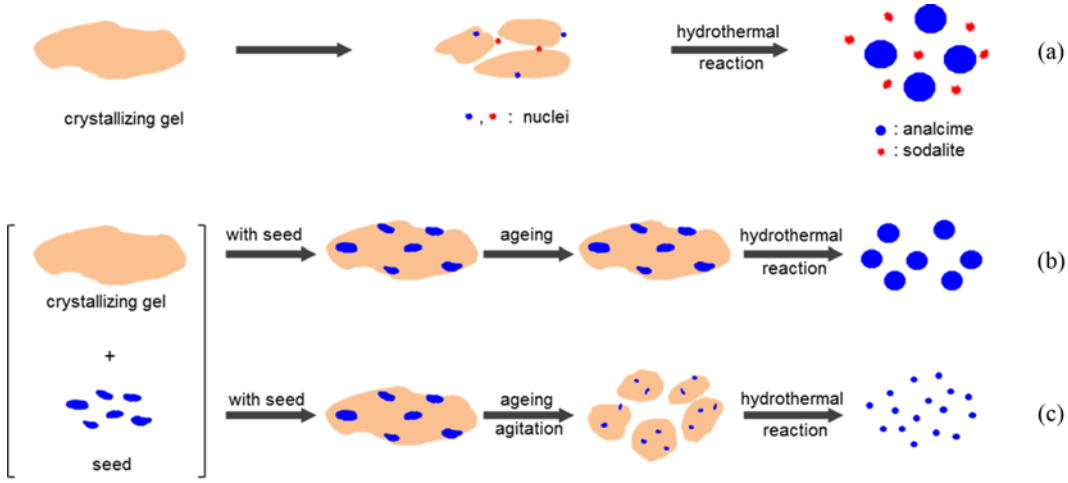
Fig. 9. SEM photos of analcime particles obtained from the synthesis mixtures containing (A) ANA_A1.0 seeds and (B) ANA_A3.0 seeds after 1 d ageing under different agitation speeds: (a) 200 rpm, (b) 300 rpm, and (c) 500 rpm. The synthesis was carried out at 170 °C for 3 h and the inserted scale bars represent 1 μm.

of the obtained particles clearly reveal smaller particles at the higher agitation speed. Specifically, for the synthesis mixture seeded with ANA_A1.0 and aged for 1 d, the analcime particles of 0.75±0.04 μm obtained with agitation at 200 rpm were reduced to 0.49±0.05 μm at 500 rpm. Similarly, for ANA_A3.0, the particles of 3.05±0.11 μm obtained at 200 rpm were reduced to 2.03±0.06 μm at 500 rpm. It can be inferred that the stronger agitation broke the seeds more effectively into nuclei, resulting in the smaller particles.

The illustrations in Scheme 1 compare the three schemes for analcime synthesis attempted in this study. Starting from an unseeded synthesis mixture, the usual steps of nucleation and crystal growth for zeolite synthesis were carried out for analcime and sodalite, respectively, producing a mixture of crystals. When the acid-treated analcime seeds were added to the synthesis mixture, the rapid consumption of the source materials for growth on the analcime seeds suppressed the nucleation of sodalite, leading to uniformly sized analcime particles. When the seeded synthesis mixture was aged under agitation for some time, the fragile seed particles were shattered into many pieces, resulting in smaller analcime particles in the subsequent hydrothermal reaction. Longer ageing time and higher agitation speed afforded smaller analcime particles.

CONCLUSIONS

A new scheme offering fine particle control has been proposed for synthesizing analcime by adding acid-treated analcime parti-



Scheme 1. Synthesis of analcime from the synthesis mixtures containing. ANA_Ax seeds through hydrothermal reaction: (a) without seed, (b) with seed, but without agitation, and (c) with seed and ageing under agitation.

cles to a synthesis mixture, ageing the mixture under agitation and then carrying out the hydrothermal reaction. Under agitation, the fragile seed particles shattered into numerous analcime nuclei on which analcime crystals steadily grew to uniformly sized particles. In conclusion, a discreet combination of acid concentration, ageing time, and agitation speed was found to be effective in controlling the size of small analcime particles with a narrow size distribution.

ACKNOWLEDGEMENTS

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Fine control of particle size by seeding and ageing under agitation in the synthesis of analcime zeolite

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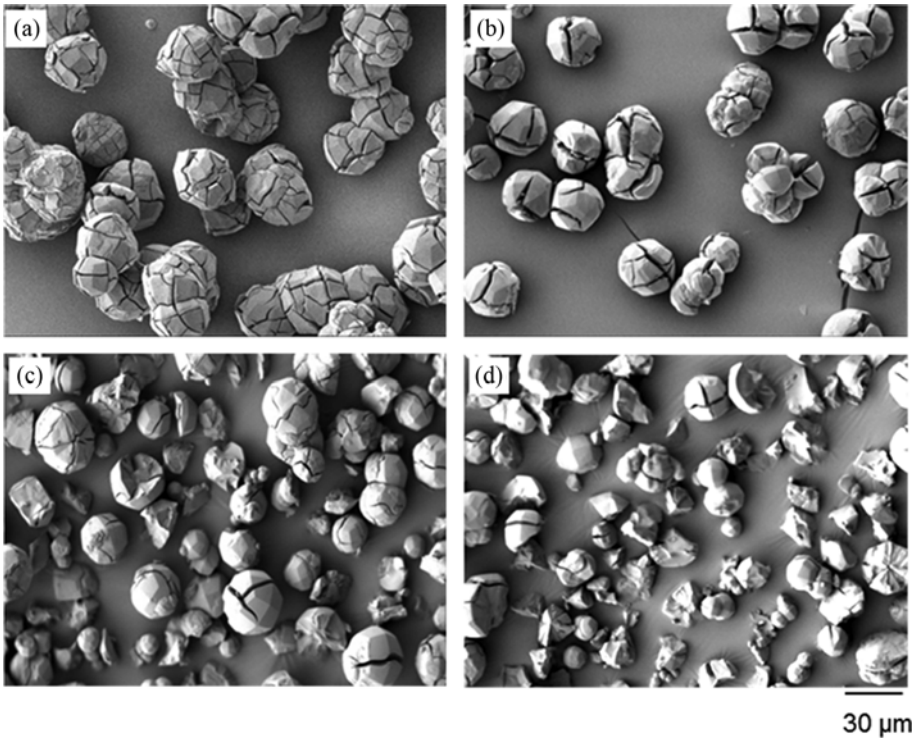

Fig. S1. SEM photos of acid-treated ANA zeolites: (a) ANA_A1.0, (b) ANA_A2.0, (c) ANA_A3.0, and (d) ANA_A4.0.

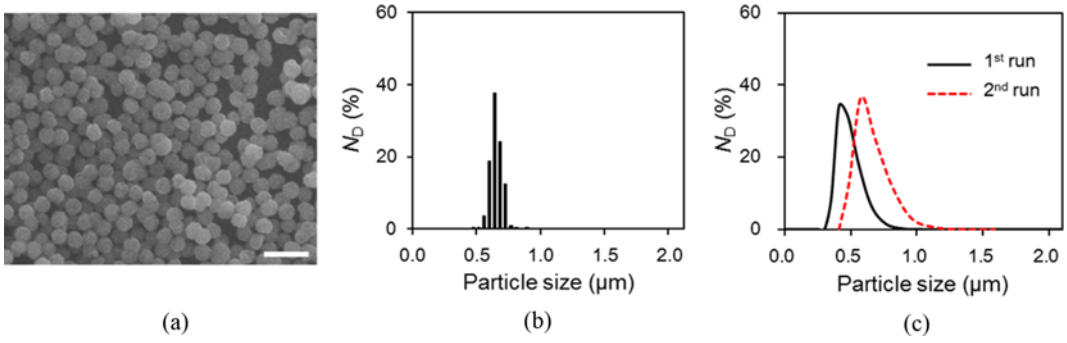

Fig. S2. Comparison of the size distributions of analcime particles obtained from the synthesis mixture containing ANA_A2.0 seeds of 1.0 wt%: (a) a SEM photo of analcime particles obtained, (b) a histogram of the size of the analcime particles calculated from the SEM photo, and (c) the size distributions of the analacime particles recorded using the PSA. N_D in (b) and (c) is the number density of particles and the inserted scale bars represent 2 μm.

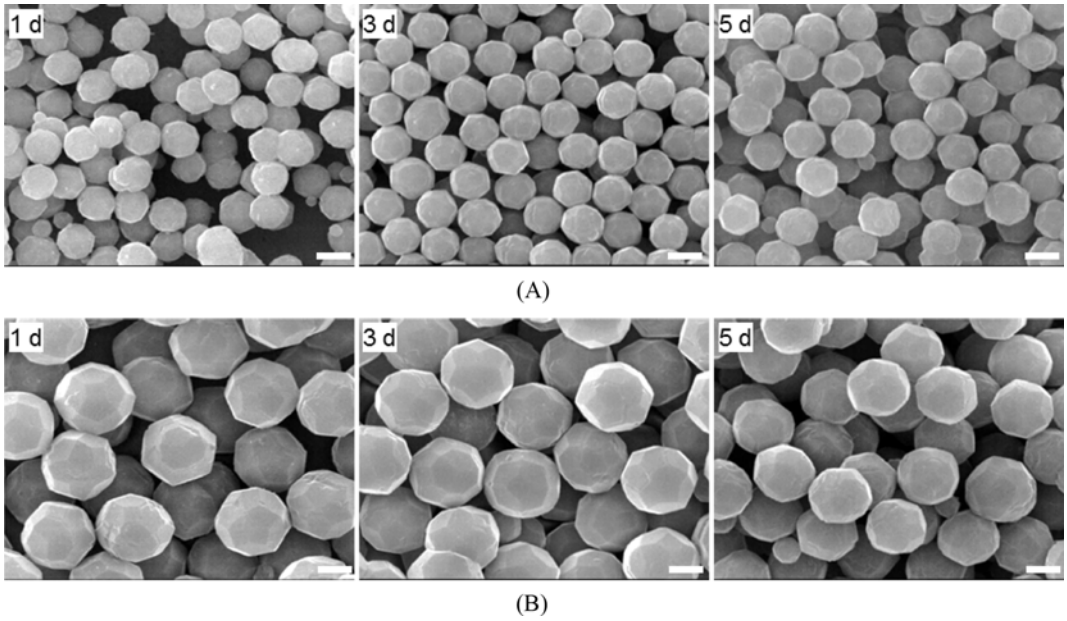

Fig. S3. SEM photos of analcime particles obtained from the seeded synthesis mixtures with ageing, but without agitation: (A) ANA_A2.0 and (B) ANA_A3.0. The inserted scale bars represent 2 μm.