Sonochemical Synthesis of Zeolite A from Metakaolinite in NaOH Solution

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Sonochemical synthesis of zeolite A has been conducted by ultrasonic irradiation of mixtures of metakaolinite and NaOH solution. The hydrothermal synthesis at conventional synthesis conditions was undertaken to determine the sonochemical reliability. The enhancement of nucleation and crystallization rate of zeolite A was achieved by ultrasound. In the ultrasonic field, zeolite A once formed in the suspension has been converted into hydroxysodalite and losod as sonicating proceeded. Comparing the results with those of conventional methods, this heterogeneous reaction was particularly accelerated by ultrasound, leading to improved reactivity of solid reactant through intensive mixing. The use of ultrasound enables us to prepare well-dispersed fine zeolite A particles with mean particle size of around 1 μm. The cation exchange capacity values of the products increased as the synthesis reaction for zeolite A proceeded. The high solid concentration in the suspension, however, hindered the ultrasound from intense agitating, resulting in the decrease of zeolite A yield. [doi:10.2320/matertrans.M2010191]

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1. Introduction

Zeolite is a family of hydrated aluminosilicate minerals that contain alkali and alkaline earth metals. Zeolites are noted for their ability toward ion exchange and reversible dehydration.¹² They have a structure that encloses interconnected cavities occupied by large metal cations (positively charged ions) and water molecules. Properties of zeolites are exploited through commercial productions with particular structural and chemical features. Zeolites are used for fluidized catalytic cracking (FCC) of petroleum refining, drying reagents of gases and liquids and selective molecular adsorbent for pollution control.³⁻⁵ In such usage, artificial zeolites are normally employed. Commercially, due to the diverse applications of synthetic zeolites, which are prepared by hydrothermal crystallization process, the degree of control over their preparation and properties bears importance even though it gives various zeolites of high chemical homogeneity and purity. In this respect, the nucleation, crystal growth and the resulting particle size are especially important. The reactant molar ratio, reaction time and temperature in hydrothermal reaction are the main factors determining the types and properties of zeolites.⁶

It has been well recognized that the ultrasonic irradiation causes cavitation in an aqueous medium where the formation, growth and collapse of microbubbles occurred.⁷ This can stimulate the reactivity of chemical species involved, resulting in the acceleration of the heterogeneous reactions between liquid and solid reactants. These processes, involving dissolution and precipitation of solids through particle size reduction and surface activation by intensive stirring, have also been identified.⁸⁻¹⁰ Recently, the effects of ultrasound have also been investigated for different cases involving polymerization reactions and the syntheses of various amorphous and crystalline materials. Although, the benefit of using ultrasonic irradiation was confirmed, in some cases, as promising tools to assist the synthetic reactions to prepare fine ceramic powders, inorganic materials and catalysts,¹¹⁻¹⁴ the reaction mechanism in the aqueous suspensions is not fully understood.

The uses of ultrasound for the synthesis of zeolite A have been applied previously. Park et al.¹⁵ proposed that zeolite A could be obtained from activated kaolin with an aid of ultrasound. Andac et al.¹⁶ synthesized zeolite A from sodium aluminosilicate solution in the presence of ultrasound. Both studies, however, were conducted in an ultrasonic water bath, i.e., commercially available ultrasonic cleaner in which the ultrasonic energy was transmitted to the reaction vessel through distilled water in the bath. In these indirect methods, therefore, the time to be required for the nucleation and crystallization of zeolite A in the suspension would be retarded, resulting in the low or partial crystallinity of final products.

Compared the previous work, this study used an ultrasonic homogenizer in order to introduce ultrasound directly into the reaction mixture of NaOH and metakaolinite. The experimental variables that influence the zeolite A synthesis such as sonicating time and solid concentration of the suspension have been explored. These sonochemical reactions were characterized by determining the crystallinity, morphology, particle size distribution (PSD) and cation exchange capacity (CEC) of the reaction products. The products are compared to those obtained by performing conventional hydrothermal synthesis in similar synthetic conditions.

2. Experimental

The starting sample of this work was metakaolinite powder, which could be obtained by heating kaolinite (Al₂Si₂O₅(OH)₄) in air at 650°C for 2h. The powder obtained consisted of agglomerates of platy and fine particles with mean particle size of 27.8 μm as shown in Fig. 1. Reagent grade NaOH pellets supplied by Wako Chemicals were used as the sodium source.

All the experiments of this work were conducted in batch mode. A 5.5 g of the powder was dispersed in a HDPE vial (ϕ50 mm × 80 mm(h)) with 85 ml of NaOH solution (3.5 mol/L) prior to ultrasonic irradiation. The ultrasound

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equipment was from VCX-1500, Ultrasonic Homogenizer, Sonics & Materials Inc., which produces acoustic waves at a frequency of 20 kHz with the maximum power of 1500 W.

The sonic horn made of titanium alloy (tip diameter \(d = 20 \text{ mm}\)/length \(l = 60 \text{ mm}\)) was driven by a PZT transducer, and it was dipped into the suspension around 20 mm from the bottom of the vial. The suspension was subjected to irradiation of ultrasound at the optimum sonicating conditions; the sonicating power and amplitude were adjusted to provide optimum power output of the generator. The irradiating time was set in the range from 15 to 240 min.

During the ultrasonic treatment, it was noted that the temperature of the suspensions increased to \(75^{\circ}\)C within 10 min and the temperature of the suspension was not changed further. After sonicating at a preset time, the suspension was centrifuged and the solid phase (powder) was washed with distilled water three times. Subsequently the powder was rinsed with pure ethanol and dried at \(80^{\circ}\)C for 24 h. The effect of solid/liquid ratio on the synthesis reaction was also investigated at different sample weight (w/v ratio).

In order to confirm the sonochemical effect, heat treatment of the suspension was undertaken under the similar conditions (\(75^{\circ}\)C) as those of ultrasonic treatment.

To characterize the phases and crystallinity of the products obtained from the suspension with and without ultrasound, a X-ray diffractometer (XRD, RINT-2000, Rigaku) using Cu-K\(_\alpha1\) radiation in the 2\(\theta\) range of 5\(^{{\circ}}\)–65\(^{{\circ}}\) was used. The morphology, crystallinity of zeolite A crystal and PSD of the products were determined by scanning electron microscope (SEM, SEM-4100, Jeol) and laser light scattering particle size analyzer (PSA, Mastersizer 2000, Malvern), respectively. The infrared absorption of the products was analyzed by Fourier-transform infrared spectrometer (FT-IR, Nicolet 380, Thermo-Electron Co.) using conventional KBr method. CEC of the products was measured by Schollenberger method using ammonium acetate.  

3. Results and Discussion

It has been suggested that each collapse of microbubbles caused by acoustic cavitation may create a nucleation site analogous to that from a trace particle or a surface imperfection. Furthermore, it is understood that high power ultrasonic irradiation is very effective in homogenizing the reactants in the suspension, leading to the improvement of reactivity of both solid and liquid by the simulation of their active surface.

The synthesis of zeolite A was carried out with and without ultrasonic irradiation at various times. Figure 2 shows the XRD patterns of the products obtained from the suspension sonicated for various times (a) 15 min, (b) 30 min, (c) 60 min, (d) 120 min, (e) 180 min and (f) 240 min.)
slightly and other phase corresponding to hydroxysodalite (HS, $Na_4Al_3Si_3O_{12}(OH)$, JCPDS 11-0401) was detected in the product obtained at the extended sonicating time (180 min), implying that the zeolite A once synthesized in the suspension started to convert into other phase as sonication proceeded. Similar trends could be observed in conventional hydrothermal syntheses where zeolite Na-P1 was formed at low alkaline concentrations and HS instead of zeolite A at high alkaline concentrations, since zeolite A is metastable and tends to transform thermodynamically to more stable phases.\(^{19}\)

In order to confirm this sonochemical effect, hydrothermal synthesis was conducted at similar conditions (Fig. 3). It is noted that highly crystalline zeolite A could be successfully prepared at both synthesis conditions, irrespective of whether ultrasound was applied or not. In the product sonicated for 240 min, however, the conversion of zeolite A to other phases such as HS and losod ($Na_{12}Al_{12}Si_{12}O_{48}xH_2O$, JCPDS 31-1269) was clearly observed. This indicates that ultrasonic method is superior to the heating method reducing the reaction time required till zeolite A is converted into HS and losod in the suspension. Moreover, it is commonly understood that ultrasonic irradiation leads improved reactivity of solid reactants by reduction of particle size and creation of surface defects thereby increasing the reactive surface area.

Figure 4 shows the relative crystallinity ($I/I_0$) of zeolite A obtained with (UI) and without ultrasound (MS). XRD analysis was mainly applied to evaluate the crystallinity of zeolite A crystals formed in all of the products. The relative crystallinity of zeolite A was determined by taking into account the intensity of commercial synthetic zeolite A (Colite-P, Cosmo Fine Chem., Korea), which was assumed to have 100% crystallinity. The relative crystallinity of the products was calculated by eq. (1).
Crystallinity \( (I/I_0) \)

\[
= \frac{\sum \text{intensity of XRD peak of product}}{\sum \text{intensity of XRD peak of standard zeolite A}}
\]  

It can be clearly seen that much earlier nucleation and higher crystallization rate of zeolite A was achieved in the presence of ultrasound. The results can be also explained by the effect of ultrasound described above, i.e., the use of ultrasound led to substantial reductions in induction time and overall completion time for the reaction. Comparing these results with those of previous works cited above, it can be possible to say that this direct ultrasonic method is much favorable for the synthesis reaction of zeolite A in terms of the time to require till zeolite A is formed in the suspension.

Figure 5 shows the FT-IR curves of the products obtained from the suspension sonicated at different times. The curves for the starting sample and commercial zeolite A were also presented for comparison. For the starting sample, the broad band located at 1070 cm\(^{-1}\) and 798 cm\(^{-1}\) could be assigned to the stretching Si-O bonds in SiO\(_2\) and Al-O bonds in Al\(_2\)O\(_3\), respectively.\(^{20}\) The band at 466 cm\(^{-1}\) related to the internal bending or stretching of T-O-T (T = Si or Al) bridge of aluminosilicates. Thus no appreciable differences can be seen in all of the products. These characteristic bands, consequently, proved the conversion of kaolinite into metakaolinite takes place by heating.

In the curves obtained for the reaction products, the band at 798 cm\(^{-1}\) of starting sample decreases and almost disappears whereas the band at gradually as sonicating time increases. The band at around 557 cm\(^{-1}\) is closely related to the formation of double four-membered rings (D4R) in zeolite structure.\(^{21}\) In addition, the band at 1070 cm\(^{-1}\) was shifted to around 1000 cm\(^{-1}\), which is an important assignment of Si-O-Al bonds in TO\(_4\) tetrahedra in zeolite or HS structure, strongly suggests that SiO\(_2\) and Al\(_2\)O\(_3\) of the starting sample were transformed into aluminosilicates structure with an aid of ultrasound.\(^{22}\) On the other hand, the bands of weak intensity detected at 721, 694 and 663 cm\(^{-1}\) in the product obtained at an extended sonicating time of 240 min are in good agreement with the characteristic bands for HS structure.\(^{23}\)

Ultrasonic irradiation would also facilitate the preparation of very fine and well dispersed crystals. Figure 6 shows the SEM photographs and their PSDs of the 120-min sonicated and 240-min heated products, respectively. The zeolite A crystals produced in the presence of ultrasound showed reduced particle size over conventionally produced crystals.

Figure 7 shows the variation of CEC of the products obtained from the suspension with and without ultrasound for various times. It can be seen that, in the presence of ultrasound, the CEC value increases rapidly in the product obtained at 60 min. It increases further as sonicating proceeds, however, no appreciable changes could be observed in the products obtained at prolonged sonicating time.
analyses proved that zeolite A started to form in the product obtained from the suspension sonicated for 30 min. The intensity of the peaks increases markedly as sonication proceeds. At the extended sonication time up to 180 min, on the contrary, different types of zeolites such as HS and losod were produced. Comparing the results with conventional methods, this heterogeneous reaction was particularly accelerated by ultrasound; much earlier nucleation and higher crystallization rate were achieved.

In the zeolite A crystals produced in the ultrasonic field showed narrow PSD with mean particle size of around 1 μm. The CEC values of the products increase as synthesis reaction for zeolite A proceeds. The solid/liquid ratio (w/v) of 1.0 was found to be the suitable for the preparation of zeolite A in the presence of ultrasound. It indicates that there exists an optimum solid concentration of the suspension in which the collision of particles increases, resulting in the improvement of zeolite A yield.

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4. Conclusion

Zeolite A was synthesized with an aid of ultrasonic irradiation of NaOH solutions containing metakaolinite. The experimental variables that influence the zeolite A synthesis such as sonicating time and solid concentration of the suspension have been evaluated. The conventional hydrothermal synthesis at the similar synthesis condition was also undertaken to determine the sonochemical effect. XRD