Synthesis of Zeolite-A Using Silica from Rice Husk Ash

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We describe the synthesis of zeolite-A using rice husk ash (RHA) as starting material. Synthesis comprised alkali activation at low temperature (<100 °C) using NaOH as reagent. We investigated the effect of experimental conditions on zeolite synthesis from RHA. The process was studied as a function of NaAlO2 addition, NaOH concentration, temperature, and reaction time. A stirred batch reactor was used under the following reaction conditions: SiO2/Al2O3 molar ratio, 1.7–2.8; NaOH concentration, 2–6 M; temperature, 50–80 °C; reaction time, 0–48 h. The obtained solids were identified by X-ray diffraction and characterized by scanning electron microscopy; specific surface areas and cation exchange capacity values were also determined. Concentrations of Si and Al in the solution were analyzed to monitor the reaction process. Single zeolite-A can be synthesized from RHA under all our experimental conditions. We proposed the formation mechanism of zeolite-A from RHA. The silicate ion dissolves in NaOH solution from RHA and reacts with aluminate in the solution to form aluminosilicate, from which zeolite-A crystals are generated. The high crystallinity was obtained rapidly when SiO2/Al2O3 ratio, NaOH concentration and temperate were high in this experimental conditions.

Introduction

Zeolites are hydrated crystalline aluminosilicates with open three-dimensional framework structures, comprising a SiO44− and AlO45− tetrahedral linked by a shared oxygen atom to form regular intracrystalline cavities and channels of atomic dimensions. Thirty-nine naturally occurring zeolite species have been recorded and >100 species have been synthesized (Dyer, 1988). Zeolite synthesis has been much studied because of their abundant use as catalysts, ion exchangers, adsorption agents, and water softeners. Hydrothermal synthesis of aluminosilicate zeolites involves a few elementary steps in which a mixture of silicon and aluminum compounds, metal cations, organic molecules, and water is converted via an alkali-supersaturated solution into a microporous crystalline aluminosilicate (Feijen et al., 1994). Most silica sources used in zeolite synthesis are commercially available as solutions, gels, fumed solids, colloids, and organic derivatives (e.g., tetraethylorthosilicate) but they are expensive. Zeolite synthesis from low-cost silica-alumina sources has been the aim of many studies, e.g., fly ash, kaolinite, diatomite, perlite, and waste porcelain (Basaldella et al., 1993; Kolay et al., 2001; Querol et al., 2002; Lin et al., 2003; Sanhueza et al., 2003, 2004; Alkan et al., 2005; Chaisena and Rangrsriwatanan, 2005; Fernandez Machado and Miotto, 2005; Wajima and Ikekami, 2007; Wajima et al., 2007; Wang et al., 2007).

In this study, rice husk ash (RHA) was used as the silica source for zeolite synthesis. Rice is one of the major cultivated plants; world production in 2002 was 576 million tons. Rice husk is agricultural waste, a byproduct of rice milling. The annual amount of discharged rice husk in Japan is 2 million tons. Some rice husk is used for fuel, brick making, animal feed, and fertilizer, but most is considered waste, causing disposal problems. Like most other biomass materials, rice husk contains a high amount of organic volatiles, and is recognized a potential source of energy (Kaupp, 1984). Gasification of rice husk is an effective technology option for use as a renewable energy source. About 20% of RHA is amorphous silica, making it economically attractive. Chemical analysis shows that a white variety of RHA can contain 70–99% silica. The large amount of silica freely obtained from rice husk provides an abundant and cheap alternative of silica sources for many industrial uses, including zeolite synthesis.

Preliminary efforts in zeolite synthesis were made using RHA, e.g., mordenite, zeolite-X, zeolite-Y. ZSM-5, ZSM-48 and zeolite-beta (Bajpai et al., 1981; Dalai et al., 1985; Wang et al., 1998; Prasetyoko et al., 2006; Vempati et al., 2006). Our objective was preparation of zeolite-A. The latter possesses unique structural properties, and is extensively used in adsorption and ion-exchange processes (e.g., drying gasses and liquids).
Zeolite-A (Na\(_{12}\)Al\(_{12}\)Si\(_{12}\)O\(_{48}\)·7H\(_2\)O) has a Si/Al molar ratio of one, and hydrophilic properties. The reaction caused by adsorption of water vapor is exothermal, and the heat of this reversible chemical reaction can be stored. Dehydrated zeolite-A possesses a high capability for heat storage, and can be used as heat-storage material for low-grade heat sources (e.g., waste heat from an industrial plant (Fujiwara and Mizota, 2001)). Producing a large amount of zeolite-A at low cost is therefore desirable, but synthesis of zeolite-A from RHA has not been attempted. More information is needed about zeolite synthesis at low temperature (\(<100^\circ\)C) because it is less expensive than zeolite production under hydrothermal conditions (\(>100^\circ\)C).

Our objective was to investigate the formation behavior of zeolite-A during the synthesis from RHA by varying SiO\(_2\)/Al\(_2\)O\(_3\) molar ratios (Al addition), NaOH concentrations, and reaction temperature, in order to explain the reaction mechanism and the effect of reaction condition.

## 1. Experimental

### 1.1 RHA

RHA was provided by Takuma Company Ltd. RHA was ground and sieved under 42 mesh, and heated at 650°C for 2 h. Table 1 shows the chemical composition of RHA determined by the method reported by Tsubaki (1975), JIS M 8852 and JIS 8854. RHA is composed mainly of SiO\(_2\) (88.2%), followed by Al\(_2\)O\(_3\), Na\(_2\)O, K\(_2\)O and Fe\(_2\)O\(_3\).

### 1.2 Zeolite synthesis

Barrer (1982) reported that zeolite-A, zeolite-X, zeolite-P and hydroxysodalite were synthesized from Na\(_2\)O·Al\(_2\)O\(_3\)·nSiO\(_2\) (\(n = 1–6\)) gel in NaOH solution at low temperature (\(<100^\circ\)C), and high NaOH concentration promoted hydroxysodalite crystallization. Hollman et al. (1999) also reported that zeolite was synthesized from a silica extract from coal fly ash with addition of aluminate, and the obtained phases were Na-A at SiO\(_2\)/Al\(_2\)O\(_3\) = 1.6, Na-X at SiO\(_2\)/Al\(_2\)O\(_3\) = 3.6, and Na-P at SiO\(_2\)/Al\(_2\)O\(_3\) = 4.0. According to these results, the following range of operating variables were used to synthesize zeolite-A from RHA: synthesis time, 0–48 h; SiO\(_2\)/Al\(_2\)O\(_3\) molar ratios in the starting mixture, 1.7, 2.2 and 2.8; NaOH, 2, 3 and 6 M; and reaction temperature, 50, 65 and 80°C. The experimental apparatus is shown in Figure 1; the experimental procedure is described below.

NaOH (Nacalai Tesque, Inc.) was mixed with solution containing appropriate concentrations of NaAlO\(_2\) (Wako Pure Chemical Industries, Ltd.) and H\(_2\)O. Twenty grams of RHA were added to 0.7 L of prepared solution in a 1-L Teflon vessel equipped with a stirrer. The slurry was continuously stirred (650 rpm) at 50, 65 and 80°C for 48 h. Aliquots (10 mL) of each slurry were removed at various time intervals to monitor the reaction process. Aliquots were filtered, and the concentrations of Si and Al in the filtrates were analyzed by the molybdenum blue method and EDTA-Zn back titration method, respectively. Solid residue was washed with distilled water, and dried at 110°C for 2 h. Residues were analyzed by X-ray diffraction spectroscopy (XRD) (JDX-7F, JEOL Ltd.) to identify the zeolite-A phase. The crystallinity of zeolite-A in the residues was calculated by the X-ray intensity ratio of the product to standard (4 1 0) diffraction faces. Commercial NaA zeolite (Mizusawa Industrial Chemicals, Ltd.) was the standard. Surface areas of residue were measured using a N\(_2\) gas adsorption method at −195°C by a surface analyzer (GAS-10, Yanagimoto Mfg. Co., Ltd.). Cation exchange capacities (CECs) of the residues were measured by the following method. Sample (0.1 g) was added to 250 mL of solution with 198 mg of CaCl\(_2\) and stirred for 10 min. After stirring, the solution was filtered, and the concentration of Ca\(^{2+}\) in the filtrate determined by atomic absorption spectrometry (AA-782, JEOL Ltd.) to calculate the amount of Ca\(^{2+}\) ions exchanged by zeolite.

## 2. Results and Discussion

### 2.1 Synthesis of zeolite-A from RHA

The synthesis of zeolite-A from RHA was investigated by the reaction in the solution and the proper-

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### Table 1 Chemical composition of RHA

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Content [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>88.2</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>5.1</td>
</tr>
<tr>
<td>Na(_2)O</td>
<td>0.2</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>2.6</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>0.5</td>
</tr>
<tr>
<td>Total</td>
<td>96.6</td>
</tr>
</tbody>
</table>
peaks of zeolite-A appeared, and the intensity of zeolite-A increased: a single zeolite-A phase could be obtained from RHA.

Figure 3 shows the scanning electron micrograph of residue after the alkali reaction for 48 h. Zeolite-A possesses the LTA-type framework, and the morphology of zeolite-A generally exhibits cubic particles. Figure 3 provides evidence that cubic crystals of zeolite-A (1–2 µm in size) can be synthesized from RHA.

Figure 4 shows the Si and Al concentrations in the solution and crystallinity of zeolite-A in the residue during synthesis. Al concentration in the initial solution was 360 mmol/L. After introduction of RHA to the solution, Si concentration increased initially, and reached steady state after 2 h, while Al concentration gradually decreased to zero. Crystallinity of zeolite-A was almost zero below 8 h of reaction, and then increased to approximately 80%.

Figure 5 shows the relationship between crystallinity of zeolite-A, CEC of residue, and specific surface area during synthesis. CEC of residue increased, and the change of CEC was similar to that of zeolite-A crystallization. Specific surface area of RHA was 24 m²/g, and decreased to almost 3.0 m²/g during synthesis. RHA was amorphous and easily dissolved in alkali solution. It is thought that the surface of RHA dissolved in the solution to decrease specific surface area, and then dissolved Si and Al in the solution created the precursor to crystallize zeolite-A due to the increase of CEC of residue.

From these results, we proposed the formation mechanism of zeolite-A, as shown in Figure 6. The formation mechanism of zeolite-A was considered to be consecutive reaction in three steps—dissolution, gelation, and crystallization—as reported for zeolite synthesis from fly ash by Murayama et al. (2002). First step is dissolution. After introduction of rice husk ash to the alkali
solution, Si was dissolved from rice husk ash into the solution, together with the decrease of surface area on rice husk ash. Second step is gelation. The dissolved Si was reacted with Al in the solution to create aluminosilicate precursor, and Al content in the solution gradually decreased. Si content in the solution was almost constant due to the dissolution of amorphous Si phases in RHA to the solution, indicating the decrease of broad hump in Figure 2. Final step is crystallization. The precursor was transformed into zeolite-A crystal to increase crystallinity of zeolite-A, and growth of zeolite-A crystals was not recognized to attain saturation state.

2.2 Formation behavior of zeolite-A from RHA under various conditions

The effect of SiO$_2$/Al$_2$O$_3$ ratio, NaOH concentration and temperature on the formation behavior of zeolite-A from RHA was examined.

Figure 7 shows Si and Al concentrations in the solution and crystallinity of zeolite-A in the solid during the alkali reaction when the SiO$_2$/Al$_2$O$_3$ molar ratios were (a) 1.7 and (b) 2.8. With increasing SiO$_2$/Al$_2$O$_3$, the initial Al concentration decreased due to the decrease of NaAlO$_2$ addition. In the starting solution with high Al content (Figure 7(a)), Al concentration decreased gradually, and Si concentration increased initially, reaching steady state at low concentration (about 20 mg/L) after 2 h. The crystallinity of zeolite-A was zero until 8 h, and then increased to about 60% to become saturated. After saturating crystallinity, Al content remained in the solution, because Si content is shortage to react with Al content for precursor. In the starting solution with low Al content (Figure 7(b)), Al concentration decreased rapidly, and Si concentration increased, reaching steady state at about 140 mg/L after 24 h. The crystallinity of zeolite-A increased initially, and became constant at about 80% after 8 h of reaction. The decrease of Al content in the solution was faster than in the former case, indicating that aluminosilicate precipitates rapidly as zeolite. This correlated with the results of crystallinity of zeolite-A. When Al content in the solution was completely consumed, it continued to dissolve Si from RHA to the solution without creating amorphous aluminosilicate, due to the shortage of Al content in the solution, and the Si concentration in the solution increased.

**Figure 8** shows Si and Al concentrations in the solution and crystallinity of zeolite-A in the solid during the alkali reaction when NaOH concentration was (a) 2 M and (b) 6 M. In the starting solution with low NaOH concentration (Figure 8(a)), Al concentration decreased gradually, and Si concentration increased initially, reaching steady state at low concentration (about 20 mg/L) after 2 h. In the starting solution with high NaOH concentration (Figure 8(b)), Al concentration decreased rapidly, and Si concentration increased, reaching steady state at about 140 mg/L after 24 h. The increase in crystallization of zeolite-A had the same tendency as the decrease of Al content in the solution due to the creation of aluminosilicate as zeolite. Dissolution rate is remarkably dependent on OH$^-$ concentration in alkali solution, and the amount of Na$^+$ in alkali solution dominates crystallization rate (Murayama et al., 2002), which was in accordance with our results. Dissolution and crystallization rates can be enhanced by adding NaOH for the effective synthesis of zeolite-A from RHA.

**Figure 9** shows Si and Al concentrations in the solution and crystallinity of zeolite-A in the solid at (a) 50 and (b) 80°C during the alkali reaction. In the case of low
Fig. 7  Si and Al concentrations and crystallinity of zeolite-A during the alkali reaction: SiO$_2$/Al$_2$O$_3$ = 1.7 (a) and 2.8 (b). NaOH concentration = 3 M, and temperature = 65°C

Fig. 8  Si and Al concentrations and crystallinity of zeolite-A during the alkali reaction: NaOH concentration = 2 M (a) and 6 M (b), SiO$_2$/Al$_2$O$_3$ = 2.2, and temperature = 65°C

temperature (Figure 9(a)), Al concentration decreased gradually, and Si concentration increased initially, reaching steady state at low concentration (about 20 mg/L) after 2 h. The crystallinity of zeolite-A was zero after 10 h, and then increased to 50%. In the case of high temperature (Figure 9(b)), Al concentration decreased rapidly, and Si concentration increased, reaching steady state at about 100 mg/L after 24 h. The crystallinity of zeolite-A increased rapidly to 80% at the initial stage of reaction. The increase of crystallization of zeolite-A was in good correlation with the decrease of Al content in the solution. With increasing reaction temperature, the Si content dissolved from RHA for aluminosilicate gel to form zeolite-A crystal.

In our study, maximum crystallinity of zeolite-A is about 80%. It is unclear why the crystallinity of zeolite-A is saturated to about 80%. The unburned matter can be observed in the product by SEM. This would be one of the reasons why the crystallinity does not go up to over 80%.

From these results, we hypothesize that with increasing SiO$_2$/Al$_2$O$_3$, NaOH concentration and temperature, the amount of Si dissolved from RHA into the solution increases, and promotes the reaction with Al content in the solution to create a large amount of aluminosilicate gel to crystallize zeolite-A.

Conclusion

Zeolite-A was synthesized from the raw material RHA. Formation behavior of zeolite-A from RHA was investigated under various conditions.
Single zeolite-A was obtained from RHA under all our experimental conditions. There exists three steps in the synthesis of zeolite-A from RHA: the dissolution step of Si from RHA, the gelation step of Si and Al ions in alkali solution to make aluminosilicate gel, and the crystallization step of aluminosilicate gel to make zeolite-A crystal. Formation behavior depends on initial Al concentration, NaOH concentration, and reaction temperature. With increasing the SiO$_2$/Al$_2$O$_3$ ratio, NaOH concentration and temperature, the crystallization of zeolite-A was promoted. These data demonstrate that a highly crystalline single zeolite-A product can be obtained from RHA, and can control the formation of zeolite-A from RHA.

Acknowledgments
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Literature Cited
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