

Direct synthesis of NaA zeolite from rice husk and carbonaceous rice husk ash

Hadi Nur

Catalysis Research Center, Hokkaido University, Sapporo 060-0811, Japan

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Abstract

Rice husk (RH) and carbonaceous rice husk ash (CRHA) have been used as source of silica for the synthesis of NaA zeolite. It was demonstrated that the NaA zeolite can be synthesized directly from RH and CRHA. First, RH and CRHA samples were submitted to a chemical pre-treatment using NaOH solution and then followed by mixing with aluminates solutions, and maintaining the mixture at temperature of 100 °C for 5 hours. The experimental results show that the quality of NaA zeolite from CRHA is higher than that of RH, because there is the tendency the formation of amorphous phases in NaA zeolite from RH.

Keywords: NaA zeolite; rice husk; carbonaceous rice husk ash; direct synthesis

Introduction

Zeolites have been developed into key materials in the chemical industry for wide field of applications ranging from ion exchange to the catalysis of petrochemical processes. One of them is NaA zeolite. By far the greatest amount of NaA zeolite is consumed in the manufacturing of detergents. In 1987, 375,000 metric tons of NaA zeolite were produced worldwide only for the detergent industry with forecast of 2.5 million metric tons by the year 2000 (Roland, 1989).

In these days biomass as a source of renewable energy has received continuous and increasing attention. Rice husk is one of the important biomass available globally all over the world. It is estimated that about 100 million tons of rice husk is generated annually in the whole world (Islam, 2000). In many place its disposal as waste is an environmental issue. Although it has some usage as fuel for cooking and parboiling of paddy rice in the developing country, it is neither fully nor efficiently utilized.

Zeolite is synthesized under hydrothermal

conditions, generally from aqueous alkaline gel containing silica, alumina and cations. In Indonesia, commercially prepared silica suitable for such purpose is almost nonexistent and imported silica is very expensive. Rice husk (RH) is an alternative silica source instead of the pure chemical sources earlier, because it is cheap, less selective and highly active (Ramli, 1995). RH has been used as an active silica source for the synthesis of Y zeolite (Ramli, 1995), for A, Y, ZSM-5 zeolites (Kismojohadi, 1995, Rawtani *et al.*, 1989). In their investigation, rice husk ash (RHA) has been used as a source of silica. Initially, RH is completely burned to produce carbon-free white ash. Calcination (roasting) of the RH that results in a weight loss of more than 70%, will convert the organic siliceous material of the husk into white rice husk ash (WRHA) which is considered unreactive and useless mineral silica. On the other hand, moderate roasting where there is less than 30% mass loss, yields a product with a mixture of carbonaceous material and silica (CRHA) claimed to be of no practicable interest (Fuad *et al.*, 1993). The CRHA with undesirable amount of carbon is produced cause incomplete combustion (Ramli, 1995). The aim of this work is to demonstrate how the NaA

Correspondence: Hadi Nur. Phone: +81-11-706-3713,
Fax: +81-11-706-2916.
E-mail: hadi@cat.hokudai.ac.jp.

zeolite can be synthesized directly from RH and carbonaceous rice husk ash (CRHA). The advantages of direct synthesis from RH is to reduce the step of the synthesis procedure earlier (Kismojohadi, 1995, Ramli, 1995, Rawtani *et al.*, 1989).

Materials and Methods

Materials

NaOH was from Merck, aluminum hydroxide (Al₂(OH)₃) from BDH Chemical, and deionized water. The RH and CRHA obtained from a rice mill in Seberang Perak, Malaysia.

Methods

An NaA zeolite synthesis gel was prepared using the procedure described previously with some modification (Hamdan, 1989). Synthesis runs were carried out in polyethylene bottle at autogenous pressure in the oil bath. Agitation was achieved by a Teflon-coated magnetic stirrer. The temperature of reaction mixture in the oil bath was controller by using an electronic temperature controller to an accuracy of ± 5 °C. The reaction mixtures were prepared following molar composition of 8.67 Na₂O : Al₂O₃ : SiO₂ : 562 H₂O.

Direct synthesis of NaA zeolite from rice husk (RH)

In synthesis, the quantity of RH was calculated based on its the percentage of weight loss and concentration of silica (Table 1). The silicate solution was prepared by combining 11.67 g of the RH, 11.55 g NaOH and 50 g of water. The reaction mixture was sealed in stainless steel pressure vessel and heated in an oven overnight at 150 °C at autogenous pressure. An aqueous solution of sodium aluminate; prepared separately by mixing calculated proportion of aluminum hydroxide (Al₂(OH)₃), sodium hydroxide (NaOH) and water were then added to the alkaline solution, followed by vigorous stirring while heating to ensure formation of a solution. The aluminate and silicate solutions are mixed under vigorously stirring. The mixture sealed in polyethylene bottle and heating in oil bath with stirring at 100 °C for 5 hours. The solid products were filtered, washed with distillate water,

dried overnight at 100 °C and calcined at 400 °C for 1 hour.

Table 1. The amount of NaOH and H₂O for digesting RH/CRHA and the yield of NaA zeolite.

Quantity of NaOH and H ₂ O to digest RH/CRHA				
RH	CRHA	NaOH	H ₂ O	Yield of NaA zeolite
11.67 g	-	11.55 g	50 g	3.75 g
-	2.94 g	11.55 g	50 g	4.95 g

Direct synthesis NaA zeolite from carbonaceous rice husk ash (CRHA)

The procedure is similar to that of direct synthesis of NaA zeolite from RH, but the silicate solution was prepared by combining 2.94 g of the CRHA, 11.55 g NaOH and 50 g of water. The reaction mixture was heated on hot plate to ensure formation of a solution. Before the aluminate and silicate solutions are mixed, the silicate solution is filtered. The solid is characterized by X-rays diffraction (XRD). The procedure of synthesis of NaA zeolite is depicted into flowchart in Figure 1.

Characterization

The synthesized samples were characterized by X-ray diffraction analysis using Siemens D5000 Diffractometer. The crystalline compounds were further examined with infrared spectroscopy (Mattson 6020 Model Galaxy Series spectrometer) using the KBr pellet technique. The zeolites synthesized were identified by direct comparison with the diffraction patterns (Szostac, 1992). The crystallite sizes of the samples are calculated using the Scherrer formula (Cullity, 1956),

$$B = 0.9\lambda / t \cos \theta \quad (1)$$

where B = broadening of diffraction line measured at half its maximum intensity (radians), t = diameter of crystal particle and $\lambda = 1.54$ Å. Chemical analysis carried out using EDAX Philips PV 9900. The ²⁹Si solid-state NMR experiments were performed using Varian Unity INOVA 400 spectrometer.

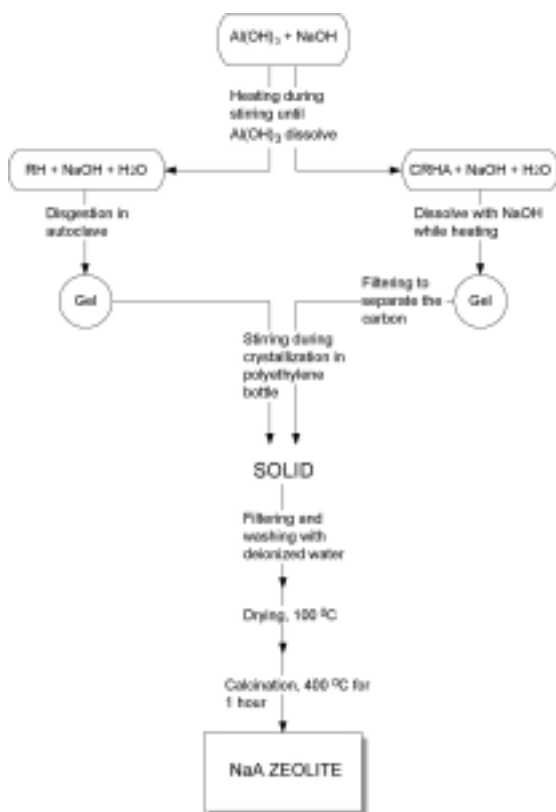


Figure 1. Schematic representation of synthesis of NaA zeolite.

The LOI (Loss of Ignition) test was carried out following the SIRIM procedure (ISO 3262-1975). About 1 g of dried sample was placed in platinum crucible and ignited in the muffled furnace at 1000 °C for 30 minutes to achieve constant mass, followed by cooling in a desiccator. The loss of ignition, as a percentage by mass, is given by the formula

$$\% \text{ LOI} = \frac{(M_0 - M_1)}{M_0} \times 100 \quad (2)$$

where m_0 is the mass of the sample and m_1 is the mass of the sample after ignition.

Silica content was determined also based on the SIRIM procedure (ISO 3262-1975). The residue obtained from LOI was added slowly with 1 mL of 50 % sulfuric acid (Merck). The crucible was heated gently until the fuming ceased and the heating was continued at 900 °C for 30 minutes in the muffled furnace. The residue was then removed

from the furnace, cooled in the desiccator and weighed (m_2). The residue was dissolved in 1 : 5 mixture of H_2SO_4 : HF (Merck) solution, and evaporated on a hot-plate until no further white fumes evolved. The crucible was ignited in the muffle furnace at 900 °C for 30 minutes, removed, cooled in the desiccator, and weighed (m_3). The silica content was calculated using the following equation:

$$\% \text{ SiO}_2 = \frac{(M_3 - M_2)}{M_1} \times 100 \quad (3)$$

Results and Discussion

Figure 2 illustrates the X-ray powder diffraction pattern for NaA zeolites was prepared from CRHA and RH as silica sources. Evidently the samples are highly crystalline and phase pure. In Figure 2b, a broad hump at low-angle appears at the baseline. It comes from an amorphous phase. These phenomena do not appear in Figure 2a. This indicates that NaA zeolite prepared from CRHA more crystalline than it prepared from RH.

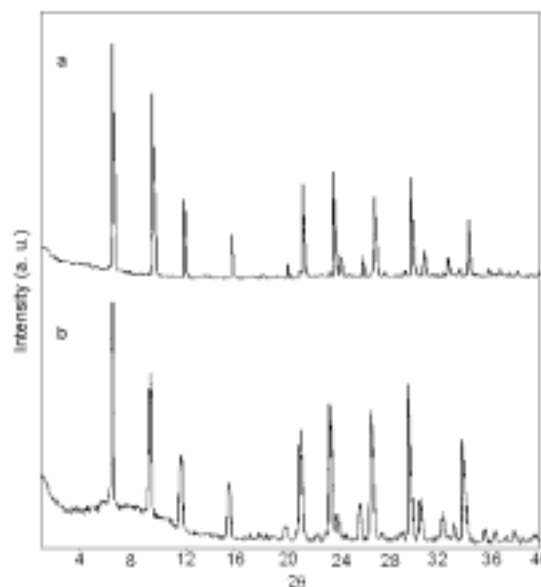


Figure 2. XRD patterns of calcined NaA zeolite synthesized from (a) CRHA and (b) RH.

As shown in Figure 2, from full width at half maximum (FWHM) of peaks also seem that the crystallite size of the NaA zeolite prepared from CRHA was bigger than that prepared from RH. The

crystallite sizes are 273 Å for NaA zeolite prepared from CRHA and 260 Å for it prepared from RH. This result is supported by infrared data. The vibration peaks of NaA zeolite prepared from CRHA were sharper compared with that prepared from RH (see Figure 3).

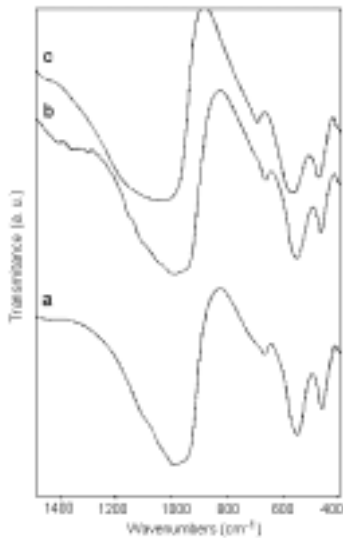


Figure 3. FT-IR spectrum of NaA zeolite synthesized from CRHA (a) after calcination, and NaA zeolite synthesized from RH (b) before and (c) after calcination at 400 °C for 1 hour.

The color of CRHA is not completely white if heating at 600 °C for 8 hours. When CRHA is heated at 700 °C for 14 and 30 hours, the colors change completely white. This indicates that at this

temperature and time the carbons remove from CRHA. If the RH is burned in the furnace with temperature increased from room temperature to 600 °C with heating rate 200 °C/h, seem that the color of the RH changes completely white after 3 hours. It was observed that combustion at lower temperature of 500 and 600 °C for 24 hours was not efficient enough to convert the ash completely white (Kismojohadi, 1995). It also depends on supply of oxygen. The XRD pattern from the CRHA as received contains crystalline silica such as cristobalite and tridymite (Figure 4). Heating the CRHA as received has no effect on the crystalline structure of the material. The CRHA has already crystallized before heating. The heating history is important because the solubility of silica in water is not simply stated, as it depends markedly on the particle size and form of the solid (quartz, cristobalite, tridymite, vitreous, etc.) and the degree of polymerization of solute, and increases with increasing alkalinity, temperature, and pressure (Barrer, 1982). The amorphous silica more soluble than cristobalite or quartz (Barrer, 1982). In this study the RH dissolves in NaOH and water under autogeneous pressure at 150 °C overnight. The quantity of RH/CRHA, NaOH and H₂O to digest RH/CRHA, and the yield of NaA zeolite are given in Table 1. The amount of silica under different weight and the combustion time of RH and CRHA are tabulated in Table 2. It showed that the concentration of silica in RH after combustion and CRHA are higher than 90%. As shown in Figure 5, a peak at 21.9 (2θ) which is assigned to cristobalite

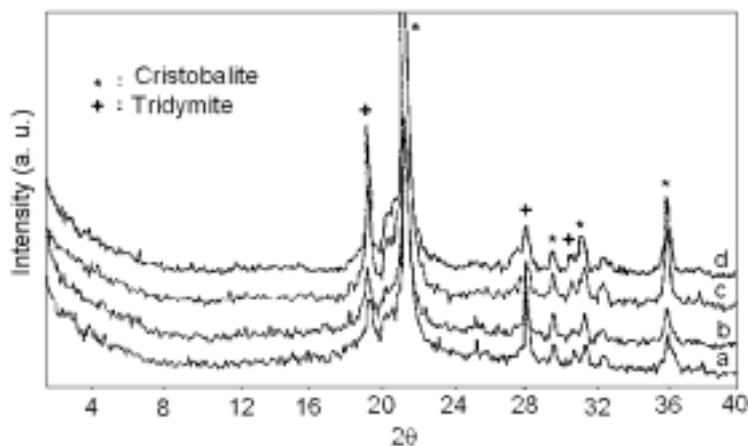


Figure 4. Variable temperature XRD patterns of CRHA (a) as received, (b) calcined at 600 °C for 8 hours, (c) calcined at 700 °C for 14 hours, and (d) calcined at 700 °C for 30 hours.

Table 2. The amount of silica under different weight and the combustion time of RH and CRHA.

Samples	Combustion Temperature	Weight of RH/CRHA	Weight loss (%)	LOI (%)	SiO ₂ (%)
RH	700 °C (6 hours)	4 g	76	-	-
RH	700 °C (24 hours)	6 g	-	2.12 ^(*)	96.91 ^(*)
CRHA	-	1 g	-	3.82 ^(*)	90.52 ^(*)

^(*)Test was carried out following the SIRIM procedure (ISO 3262-1975).

phase, is observed in the carbon after filtration. This suggested that a portion of silica be still embedded in the carbon matrix after digestion by NaOH.

The infrared spectra for NaA zeolite synthesized directly from RH and CRHA in the present case are typical of NaA zeolite material with absorption bands at 1001, 667, 554 and 463 cm⁻¹ (Szostac, 1992). Synthetic zeolites can be interpreted in terms of the spectra in the 1400-300 cm⁻¹ (Flanigen *et al.*, 1971). Calcination of NaA zeolite prepared from RH resulted in loss of the absorption bands about 1300-1400 cm⁻¹ indicating complete removal of organic species (Figure 3b). These peaks do not appear in the spectrum of the NaA zeolite prepared from CRHA (Figure 3a). The chemical analysis using EDAX shows that the chemical composition of zeolite obtained were Al = 21.6%, Si = 24.98% and Na = 8.29%. The color of NaA zeolite synthesized directly from RH is still yellowish although calcined at 400 °C for 1 hour. It probably comes from Fe₂O₃. Rawtani *et al.* found that their RH contains 0.35% Fe₂O₃ (Rawtani *et al.*, 1989).

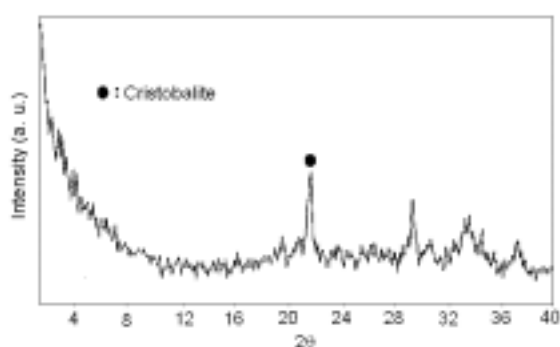


Figure 5. XRD pattern of carbon after filtration. The peak marked by dot in the pattern is from silica still remained in the carbon.

The ²⁹Si MAS NMR spectrum of NaA zeolite direct synthesis from RH consists of a single peak

at -89.21 ppm from TMS (spectrum is not shown). This indicates that NaA zeolite contains only one kind of ²⁹Si site: silicon surrounded by four aluminums in strictly ordered distribution that obeyed Loewenstein rule. The Si/Al ratio is therefore 1.

Conclusions

It was shown that NaA zeolite can be synthesized directly from rice husk (RH) and carbonaceous rice husk ash (CRHA). The experimental study on direct synthesis of NaA zeolite showed that pure and highly crystalline NaA zeolite can be obtained from CRHA. The quality of NaA zeolite obtained from CRHA is considered higher than that of RH because there is the tendency the formation of amorphous phases in NaA zeolite from RH.

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