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Synthesis of zeolite beta with pretreated rice husk silica and its transformation to ZSM-12

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ABSTRACT

Silica with 98% purity was prepared from rice husk by acid leaching and used as a silica source for the syntheses of zeolite beta (Beta) under hydrothermal conditions with gel Si/Al ratios of 8, 13, 15, 20, 50, 100, 150, and 200. Based on powder X-ray diffraction patterns, samples with gel Si/Al ratios of 8–20 contained only the pure phase of Beta and the highest relative crystallinity was observed in the Beta with gel Si/Al ratio of 13. This sample was further characterized by scanning electron microscopy, particle size analyzer and N_2 adsorption analysis. The Beta particles were sphere shaped with the average particle size of 1.5 μm and a surface area of 670 $m^2\ g^{-1}$. The samples with gel Si/Al ratios ranging from 50 to 200 showed mixed phases of Beta and ZSM-12, and the latter phase was more dominant as the Si/Al ratio increased.

1. Introduction

Rice husk is composed of both organic (about 75–80%) and inorganic components (about 20–25%) [1]. After the combustion to remove organic content, the ash contained silica with a purity of about 90% [2]. The purity of rice husk silica (RHS) could be improved by leaching out inorganic components in the husk such as oxides of calcium or aluminium with mineral acid before incineration [1,3]. The RHS could be used as a silica source for preparation of a number of porous materials such as MCM-41 [4], zeolite LSX [3], and zeolite ZSM-5 [5,6]. This work focuses on the utilization of RHS as a silica source for the synthesis of zeolite beta in proton form (H-Beta).

The general formula of Beta in sodium form is $Na_n\{Al_nSi_{64-n}O_{128}\}$, $n < 7$. It has a three-dimensional large pore with a diameter of 0.76 nm × 0.64 nm [7]. Na-Beta could be synthesized by hydrothermal method with various silica sources and organic templates [8] then the procedure followed by exchanging with ammonium aqueous solution to form H-Beta. The H-Beta is of interest as a catalyst in the conversion of organic chemicals due to its thermal and chemical stability, shape selectivity, and high acidity. The acidity is an important property of catalytic supports for metal such as platinum and palladium, because it enhances the electron-deficiency of the metal. The amount of acid sites and the hydrophilic/hydrophobic properties of the microporous material can be manipulated by controlling the Si/Al ratio.

Here we report the syntheses of H-Beta with amorphous RHS and a tetraethylamonium hydroxide (TEAOH) template by the hydrothermal method with gel Si/Al ratios ranging from 8 to 200. The synthesized products were characterized by powder X-ray diffraction (XRD) to confirm the formation of the Beta structure, compare the relative crystallinity and determine the crystal size. The acid amount in Beta was determined by X-ray fluorescence (XRF). The sample with only the pure BEA phase and the highest relative crystallinity was further analyzed with N_2 adsorption measurement, scanning electron microscopy (SEM), and a laser diffraction particle size analyzer (DPSA).

2. Experimental

2.1. Materials and chemicals

Rice husk was obtained from a local rice mill in Lampang Province, Thailand. Chemicals for the RHS preparation and Beta syntheses were hydrochloric acid (37% HCl, Carlo Erba), tetraethylammonium hydroxide (40 wt% TEAOH, Alfa), sodium chloride (NaCl, Ajax Fine Chem), potassium chloride (KCl, Ajax Fine Chem), sodium hydroxide (98% NaOH, Prolabo), and sodium aluminate (55–56 wt% $NaAlO_2$, Riedel-de Haen).

2.2. Preparation of rice husk silica (RHS)

RHS (with 98% purity) was prepared by a procedure described elsewhere [3]. Briefly, the rice husk was leached in 3 M HCl under the reflux conditions for 6 h to remove traces of other inorganic content besides silica, washed until the pH of

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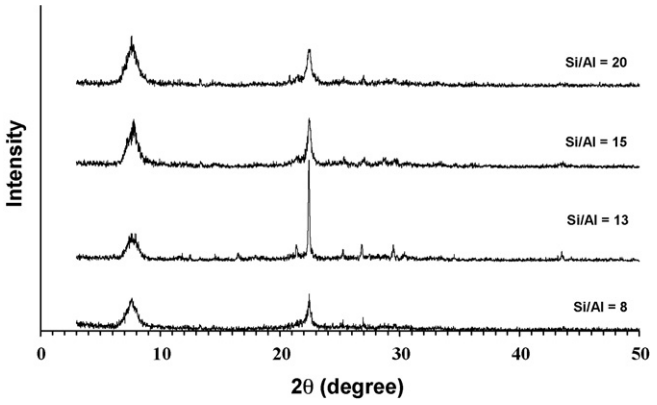

Fig. 1. XRD pattern of synthesized products with gel Si/Al ratios of 8–20.

the rinsing solution was ~7, and pyrolyzed at 550 °C. The obtained silica was in amorphous phase as indicated by XRD, similar to that in the literature [3].

2.3. Synthesis of zeolite beta

Zeolite beta in sodium form (Na-Beta) was synthesized by a method modified from the literature [9] with a gel Si/Al ratio varied from 8 to 200 and TEAOH was used as a template reagent to assist the formation of the zeolite framework. The RHS was dissolved in a NaOH solution before the addition of TEAOH. Then a solution of sodium aluminate with the desired Si/Al ratio was added and the mixture was stirred for 4 h. The obtained gel was crystallized in a teflon-lined autoclave at 135 °C for 3 days and quenched in cold water. The product was separated by centrifugation, washed until the pH of the rinsing solution was ~9, and dried at 100 °C for 24 h. Finally, the template was removed by calcination at 550 °C for 6 h. All samples were characterized by XRD (Bruker AXS Diffractometer D5005) and only samples with pure Beta phase were converted to proton form (H-Beta). The Na-Beta zeolite was three times exchanged with 20 wt% ammonium nitrate (NH_4NO_3) solution, each time for 8 h at 80 °C to produce NH_4-Beta. After separation by centrifugation, the NH_4-Beta was washed with distilled water, dried at 110 °C overnight and calcined in air at 400 °C for 3 h to convert to H-Beta.

2.4. Characterization of zeolite beta

The samples, after the template removal, were analyzed by XRD using Cu Kα (1.54 Å) radiation, 2θ scan from 3° to 50°. The relative crystallinity of the samples with a pure NaBEA phase was determined by comparing the total area of the major XRD peaks [9,10] and the sample with the highest total peak area would give a relative crystallinity of 100%.

The Si/Al ratios were determined by X-ray fluorescence (XRF, EDS Oxford Instrument ED 2000). The samples and synthetic calibration standards for XRF analysis were prepared by borate-fusion technique [11]. The flat sample disks were bombarded with X-ray generated with a high voltage of 40 kV and current of 30 mA. The quantities of oxides of silicon and aluminum were determined with a standard procedure and the acidities were calculated based on XRF measurements.

The morphology of the H-Beta with highest the crystallinity was studied by SEM (JEOL JSM-6400) and the particle size distribution (PSD) was measured by a laser diffraction particle size analyzer (DPSA, Malvern Instruments, Mastersizer 2000).

The N_2 adsorption–desorption isotherm was obtained by a Micromeritics ASAP 2010 (Autosorb-1 series). Before measurement, each sample was degassed at 300 °C for 3 h. The BET surface area was determined in the P/P_0 range of 0.01–0.3.

3. Results and discussion

3.1. XRD characterization

After calcination, the synthesized products with gel Si/Al ratios ranging from 8 to 200 were characterized by XRD. The products with pure Beta phase were transformed to H-Beta and characterized again with XRD. The gel Si/Al ratios that gave pure Beta phase were 8, 13, 15 and 20 and their spectra of the H-Beta are shown in Fig. 1. The spectrum contained large peaks of Beta at 7.8° and 22.4° along with small peaks similar to those of Beta synthesized from the commercial silica source and the simulated Beta spectrum [12].

The relative crystallinities of H-Beta with gel Si/Al ratios ranging from 8 to 20 are displayed in Table 1. The highest crystallinity

Table 1
Relative crystallinity of HBEA with various gel Si/Al ratios ranging from 8 to 20.

Gel Si/Al ratio	Total peak area	Relative crystallinity[a]	XRD crystal size[b] (nm)
8	276.6	83	86
13	346.4	100	189
15	306.7	90	71
20	320.5	93	64

[a] Calculated from total area of peaks at $2\theta = 7.8°$ and 22.4°, relative to the highest value (gel Si/Al ratio of 13).
[b] Calculated from peak area at $2\theta = 22.4°$ of XRD pattern by Scherrer equation.

was obtained from the sample with the ratio of 13. The relative crystallinity of H-Beta decreased with increasing of gel Si/Al ratio. In addition, Table 1 also shows the crystal size of these H-Beta calculated by Scherrer's equation: $t = K\lambda/(B\cos\theta)$ where t was the averaged dimension of crystallites, K is the Scherrer constant, somewhat arbitrary value that falls in the range 0.9–1.0 (it was assumed to be 0.9 in this work), λ is the X-ray wavelength, and B is the integral breadth of a reflection (in radians 2θ) located at 2θ. The crystal size was largest in the sample with gel Si/Al ratio of 13.

The XRD pattern of samples with gel Si/Al ratios ranging from 50 to 200 are shown in Fig. 2 with that of one H-Beta exemplary XRD spectrum from the sample with the gel Si/Al ratio of 13. The samples with gel Si/Al ratios ranging from 50 to 200 showed mixed phases containing characteristic peaks of the Beta and ZSM-12 [13–15]. The phase change was indicated by a splitting of the Beta peak at 7.5°, a fading of the peak at 22.4°, and an emerging of a new peak at ~21°.

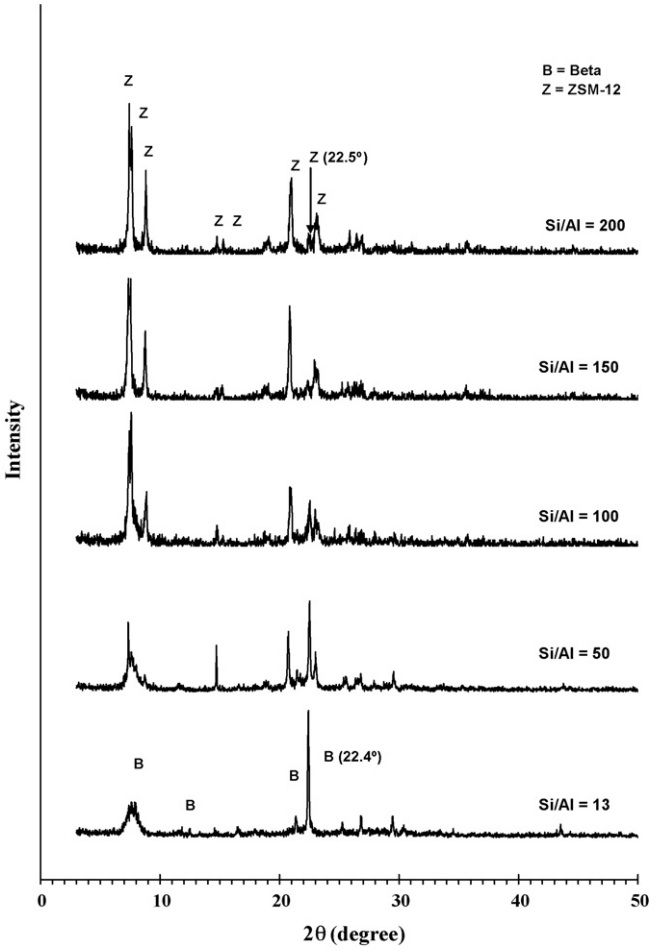

Fig. 2. XRD pattern of synthesized products with gel Si/Al ratios of 13, 50, 100, and 200.