

Synthesis and characterization of zeolite NaY from rice husk silica

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(Received 18 April 2007 • accepted 5 November 2007)

Abstract—Rice husk silica (RHS) in amorphous phase with 98% purity was prepared from a waste rice husk from rice milling by leaching with hydrochloric acid and calcination. The RHS was used effectively as a silica source for the synthesis of zeolite Y in sodium form (NaY). The zeolite in pure phase was obtained from a two-step synthetic route in which the starting gels were mixed, aged for 24 h at room temperature and crystallized for 24 h at 90 °C. The diameter of single crystal particles from a scanning electron microscope was approximately 1.0 μm , whereas the average particle diameter from laser diffraction particle size analyzer was approximately 10 μm because of the agglomeration of small crystals. Longer crystallization time in this route resulted in a mixed phase containing NaY and zeolite P in sodium form (NaP). In addition, a one-step synthetic route (no aging) was studied and the product was also a mixed phase zeolite.

Key words: Rice Husk Silica, Zeolite Y, NaY, Two-step Route, One-step Route, Zeolite P

INTRODUCTION

Rice husk, which is often considered as a solid waste from rice milling, contains approximately 70% of organic compounds and 30% of hydrate silica (SiO_2) [1,2]. In general, the rice husk can be used as a cheap energy source through combustion or for other purposes as low value material. When the rice husk is leached with mineral acid and calcined in air, white powder rice husk silica (RHS) is obtained. The RHS with high silica purity is suitable as a silica source for the production of inorganic materials such as silicon carbide and silicon nitride [3,4]. In a research field related to catalysis, RHS was used as a silica source for the synthesis of microporous materials such as zeolites [5-8] and mesoporous silica such as MCM-41 [9]. In this work, RHS was successfully used as a silica source for the synthesis of zeolite Linde type Y in sodium form (NaY).

Zeolites are microporous crystalline aluminosilicates composed of tetrahedral TO_4 units ($\text{T}=\text{Si}$ or Al) linked together by sharing oxygen atoms. The general formula of zeolites is $\text{M}^{n+}_x[\text{Si}_x\text{Al}_y\text{O}_z]\cdot m\text{H}_2\text{O}$ where M^{n+} is extra-framework cation, $[\text{Si}_x\text{Al}_y\text{O}_z]$ is zeolite framework, and $m\text{H}_2\text{O}$ is water molecules in sorbed phase [10]. Zeolites have several interesting properties that can be related to various applications such as solid acidity, ion-exchange capability, adsorption/release capability, and molecular-level pores. Zeolite NaY, the main focus in this work, is in the faujasite (FAU) family with a framework containing double 6 rings linked through sodalite cages that generate supercages with average pore diameter of 7.4 Å. There are several applications of FAU zeolites such as fluid cracking catalysts and sorbents for volatile organic removal [11].

The goal of this research was to use the RHS as silica source in the synthesis of NaY with the formula $\text{Na}_{56}[\text{Al}_{56}\text{Si}_{136}\text{O}_{384}]\cdot 250\text{H}_2\text{O}$. Two different synthetic routes, one-step and two-step, and crystallization time were investigated. The NaY products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM),

surface area analysis (BET), and laser diffraction particle size analyzer (DPSA).

EXPERIMENTAL

1. Materials for RHS Extraction and NaY Syntheses

Rice husk was obtained from a local rice mill in Lampang Province, Thailand. Chemicals for RHS extraction and NaY synthesis were hydrochloric acid (37%wt HCl Carlo-Erba), sodium aluminate (~55-56% of NaAlO_2 , Riedel-de Haën), sodium hydroxide (97%wt NaOH, Carlo-Erba), and potassium hydroxide (85%wt KOH, Ajax Fine Chem). Standard zeolites were NaY with Si/Al molar ratio 5.7 (JRC with Tosoh Crop) and NaP (Fluka).

2. Silica Extraction from Rice Husk

Rice husk was washed thoroughly with water to remove the adhered soil and dust and dried at 100 °C overnight. The dried rice husk was refluxed in 3 M HCl solution for 3 h, filtered and washed repeatedly with water until the filtrate was neutral. After the acid treatment, the rice husk was dried at 100 °C overnight and pyrolyzed in a furnace muffle (Carbolite) at 550 °C for 6 h to remove the organic contents. The obtained product, RHS, was characterized by X-ray fluorescence (XRF) and powder XRD.

3. Synthesis of Zeolite NaY

The zeolite NaY was synthesized from a seed gel and feedstock gel with a procedure modified from that described elsewhere [12]. The major difference between seed gel and feedstock gel is that the feedstock gel was prepared and used immediately without aging. Briefly, the seed gel with a molar ratio of $10.67\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 10\text{SiO}_2 : 180\text{H}_2\text{O}$ was prepared by adding Na_2SiO_3 solution to the solution of NaAlO_2 . The mixture was stirred until homogeneous and transferred into a polypropylene (PP) bottle, capped, and aged at room temperature for 24 h.

The feedstock gel with molar ratio $4.30\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 10\text{SiO}_2 : 180\text{H}_2\text{O}$ was prepared in similar fashion to that of the seed gel except that it was used immediately without aging.

The NaY synthesis was carried out by a slow addition of the seed

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gel into the feedstock gel under stirring. The mixture was transferred into a PP bottle, capped, and crystallized at 90 °C. This study compared two synthetic routes for NaY. The first route was “one-step” synthesis in which the mixture of seed gel and feedstock gel was mixed and taken directly to crystallization at 90 °C for 24 h. The second route was a “two-step” synthesis in which the seed gel and the feedstock gel were mixed and aged at room temperature for 24 h and crystallized at 90 °C at various time (22–72 h). After the crystallization, the samples were cooled down to room temperature. The solid product was separated by filtration, washed thoroughly with distilled water, and dried at 110 °C.

4. Characterization of RHS and NaY

The chemical compositions of RHS, calculated as major oxides, were analyzed by energy dispersive XRF (EDS Oxford Instrument ED 2000) with an array of 16 anodes analyzing crystals and Rh X-ray tube as target with a vacuum medium. The specific surface areas (BET), pore volumes, and pore sizes of NaY were determined by a Quantachrome (NOVA 1200e) gas adsorption analyzer, and the nitrogen adsorption isotherms were obtained at liquid nitrogen temperature. The sample was degassed at 300 °C for 3 h before the measurement.

Phase and crystallinity of the RHS and the synthesized NaY were confirmed by powder XRD (Bruker AXS diffractometer D5005) with nickel filter Cu K α radiation scanning from 4 to 50° at a rate of 0.05 degree/s. The intensity of the peak at 22.5° was chosen for the crystallinity comparison. Morphology of the synthesized NaY was studied by SEM (JEOL JSM-6400) with applied potential 10 kV. Particle size distribution was determined by DPSA (Malvern Instruments, Mastersizer 2000) with the sample dispersed in distilled water and analyzed by He-Ne laser. The standard volume percentiles at 10, 50, and 90% denoted as d(0.1), d(0.5), and d(0.9), respectively, were recorded from the analysis and used to calculate the width of the distribution. The width was calculated from the equation below:

$$\frac{d(0.9) - d(0.1)}{d(0.5)}$$

RESULTS AND DISCUSSION

1. RHS Characterization

The chemical compositions of RHS in the form of stable oxides are shown in Table 1. The major component was SiO₂ with purity approximately 98%wt along with small amounts of other inorganic oxides including Al₂O₃, K₂O, CaO, and Fe₂O₃. The silica purity was sufficient to use as a silica source for the synthesis of NaY. The silica purity of the RHS from acid-leached rice husk in this study was higher than that of the rice husk ash (RHA) obtained directly from

Table 1. Chemical components of RHS determined by XRF

Component	(%wt)
Al ₂ O ₃	00.56
SiO ₂	97.96
K ₂ O	00.06
CaO	00.98
Fe ₂ O ₃	00.02

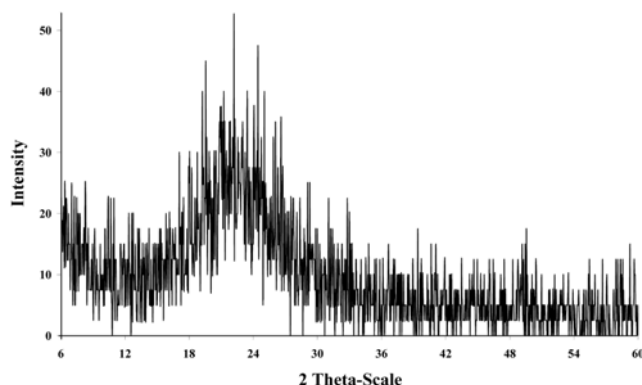


Fig. 1. XRD pattern of RHS.

rice husk combustion without leaching [7]. However, the RHA silica was still suitable for the synthesis of zeolites such as zeolite beta and zeolite ZSM-5 [6,7]. In general, RHA from pyrolysis of rice husk at high temperature contains silica in crystalline form [5], which takes a long time to dissolve in NaOH solution to form water glass for zeolite synthesis.

From the XRD pattern of RHS in Fig. 1, only a broad peak with 2θ at 22 degree, which is a characteristic of amorphous silica, was observed. This form of silica is suitable for zeolite synthesis because it dissolves easily in NaOH solution to form sodium silicate.

2. Comparison between One-step and Two-step Routes

In this work, two synthetic routes for NaY synthesis were compared: one-step and two-step. The products from both routes were characterized by XRD compared with the pattern of standard NaY. As shown in Fig. 2, two-step route gave an XRD pattern characteristic of NaY, and all peaks were similar to those of the standard NaY. Thus, the product from the two-step route contained NaY in pure phase. In contrast, the product from the one-step route gave XRD peaks that are characteristic of both NaY and NaP. It was reported that aging time was essential for synthesis of NaY (with Si/Al ratio 1.8) from kaolin [13]. The process with no aging time resulted in the formation of NaP. From this observation, the suitable method for the NaY synthesis from RHS was the two-step route and aging time of 24 h was sufficient to produce NaY in pure phase.

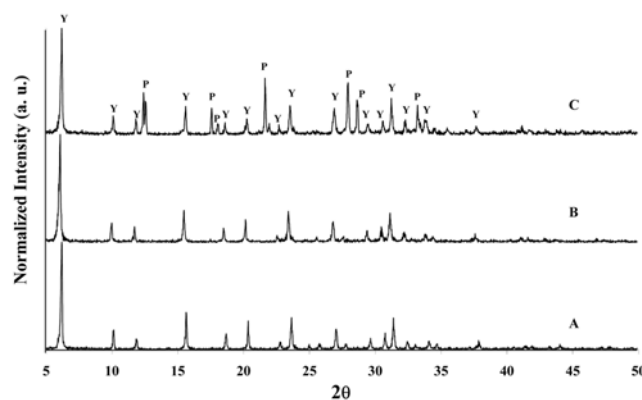


Fig. 2. Normalized XRD spectrum of NaY from one-step and two-step synthesis (A) standard Y zeolite, (B) two-step, (C) one-step; (Y=NaY and P=NaP).

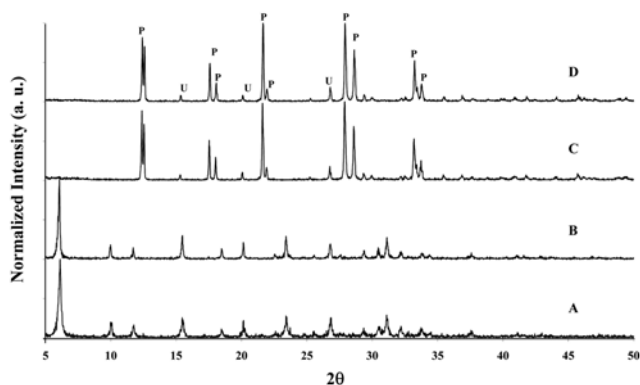


Fig. 3. Normalized XRD spectrum of NaY from two-step synthesis crystallized at (A) 22, (B) 24, (C) 48, and (D) 72 h; (P=NaP and U=unknown phase).

The mixed intermediate phase of NaY and NaP could be formed after mixing the seed gel and the feedstock gel with equilibrium in favor of NaY intermediate at room temperature; thus, aging time was required. The presence of mixed phase during crystal growth was also found in the synthesis of MFI-Type zeolites, and it was reported to be dependent on the degree of crystallization that was proposed based on the appearance of stable silicate species and the role of OH⁻ ions during the induction period [14].

3. Crystallization Time in Two-step Route

In the synthesis of NaY by two-step route, the crystallization time varied from 22 to 72 h, and the results are displayed in Fig. 3. All spectra were normalized relative to the most intense peak and the crystallinity was compared from line broadening. In the standard method [11], the crystallization time is recommended to be 22 h with no more than 2 additional h. Thus, the crystallization time was carried out at both 22 and 24 h and the product obtained from both periods displayed only spectrum characterizing NaY (Fig. 3, spectrum A and B, respectively). The spectrum of NaY from 24 h before normalization (not shown) exhibited sharper peaks with higher intensity than that from 22 h, indicating that the optimum crystallization time for the synthesis of zeolite NaY with RHS was 24 h. The relative crystallinity of NaY with 22 h crystallization time was approximately 73% compared to that with 24 h.

After 24 h, additional peaks in XRD spectrum, which are characteristic of zeolite NaP, started to appear. The intensity of NaP peaks increased with crystallization time, while that of the peaks of NaY decreased. At 48 and 72 h the main peak corresponding to NaY was not observed and the peaks of NaP were dominant (Fig. 3, spectrum C and D). Although NaP was the major product from this transformation, it was not in pure phase because peaks of an unknown phase at 15.5, 20.3 and 26.9 were also observed. The synthesis of NaP in pure phase from commercial silica suspension was reported with crystallization time of 5 days [15].

4. Textural Properties of NaY

Table 2 lists the BET surface areas, pore volumes, and average pore diameters of zeolite Y with different synthesis routes and crystallization times. The BET surface area of the product from the one-step route was lower than that of the two-step route because of the presence of zeolite P, which was a less porous phase. The presence of zeolite P was confirmed by XRD in Fig. 2 as mentioned above.

Table 2. Textural properties of synthesized zeolite Y from one- and two-step route

Sample	BET area (m ² /g)	V _p (cm ³ /g)	D _p (nm)
One-step	382.10	0.194	2.693
Two-step			
22 h	440.10	0.220	2.565
24 h	625.10	0.320	2.547
48 h	12.71	0.002	2.593
72 h	31.13	0.006	3.820

V_p=pore volume, D_p=pore diameter

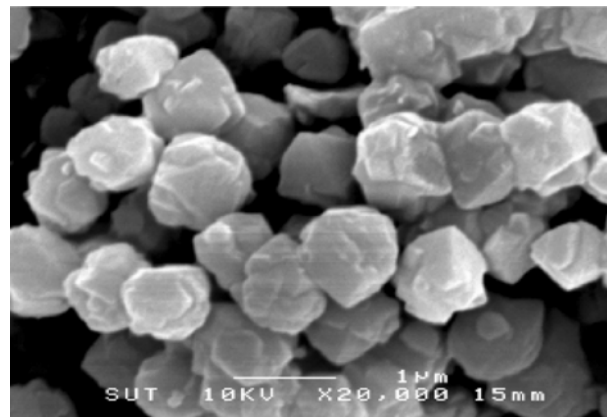


Fig. 4. SEM image of zeolite Y synthesized from RHS with magnification of ×20,000.

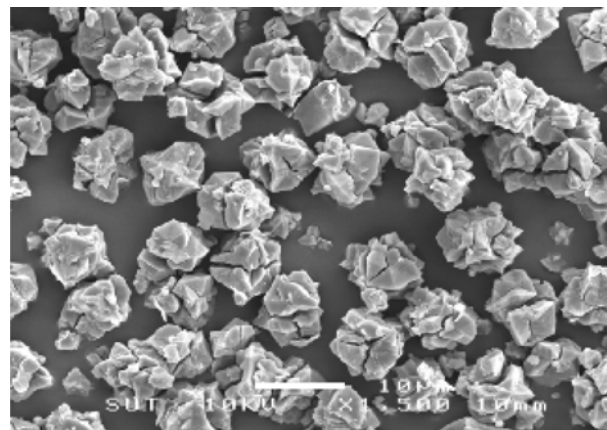


Fig. 5. SEM image of transformation products from NaY containing NaP as a major product with magnification of ×1,500.

In the two-step route, the only product observed from crystallization time of 22 and 24 h was NaY. The product from crystallization time of 24 h had surface area of 625.10 m²/g, which was higher than that obtained from crystallization time of 22 h that was 440.10 m²/g. This confirmed that crystallization for 24 h allowed more complete formation of NaY. The surface area of the products from crystallization of 48 and 72 h were much lower because the major products were zeolite P, which was a less porous phase.

5. Morphology of NaY by SEM

The SEM micrograph of NaY synthesized from RHS at opti-

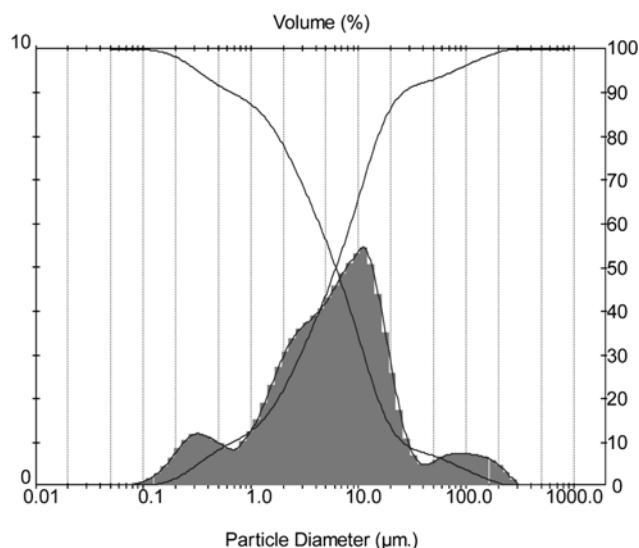


Fig. 6. Particle size distribution of zeolite Y synthesized from RHS analyzed by DPSA.

imum conditions, two-step route and 24 h crystallization time, with magnification of $\times 20,000$ is displayed in Fig. 4. The particles were uniform in size and some crystals apparently fused together to form agglomerate particles. The particle size of isolate crystal from SEM micrograph was approximately 1 μm .

As mentioned earlier, the main peak of NaY disappeared completely and the major transformation product after crystallization for 72 h was NaP. The morphology of products from this condition was also studied by SEM. As exhibited in Fig. 5, the crystal shape of NaP was apparently different from that of NaY (Fig. 4). The shape of NaP crystals could not be confirmed by SEM micrograph because most crystals had cracks through the center. The size was approximately 0.6–0.8 μm , larger than that of zeolite P prepared from commercial silicate [15].

6. Particle Size Distribution of NaY by DPSA

The result from DPSA analysis was the particle size distribution and the statistics of distribution calculated from the results using the derived diameters, an internationally agreed method of defining the mean and other moments of particles size [16] (British Standards; BS2955:1993). The percentage of volume sample that was under a certain particle size band (% under) at 10, 50, and 90% was 0.66, 6.18, and 25.93 μm , respectively. The width of distribution was 4.09 μm . The particle size distribution in all ranges by DPSA is displayed in a histogram in Fig. 6, revealing that the obtained products were not homogeneous in size. The average particle size from DPSA was approximately 15 μm . This average was different from the size of isolate crystals from SEM because several crystals fused together to form large particles. This information showed homogeneity of zeolite particles, which could be of use for designing applications of the material.

CONCLUSIONS

RHS in amorphous phase with 98% purity was prepared by leaching rice husk with HCl acid and calcination, and used as silica source for the synthesis of zeolite NaY. The NaY in pure phase was obtained from two-step synthetic route in which starting gels were mixed, aged for 24 h at room temperature and crystallized for 24 h at 90 °C. The diameter of single crystal from a scanning electron microscope was approximately 0.6–1.0 μm , whereas the average diameter of zeolite particles from the laser diffraction particle size analyzer was approximately 10 μm . When the crystallization time was longer than 24 h, NaY slowly transformed to zeolite NaP.

ACKNOWLEDGMENTS

Funding for this research was from Suranaree University of Technology, Thailand Research Fund (Contract number MRG4780147) and National Synchrotron Research Center, Thailand (Grant 2-2548/PS01).

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