

PROPERTIES OF SILICA FROM RICE HUSK AND RICE HUSK ASH AND THEIR UTILIZATION FOR ZEOLITE Y SYNTHESIS

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Recebido em 21/12/10; aceito em 22/3/11; publicado na web em 10/6/11

This study compared properties of silica (SiO_2) from rice husk (RH) and rice husk ash (RHA) extracted by acid- and heat-treatment. The SiO_2 from RH was in amorphous phase with nearly 100% purity while that from RHA was in crystalline phase with 97.56% purity. Both extracted SiO_2 were used in the synthesis of zeolite NaY but that from RH was better due to the efficiency in product recovery and simplicity of extraction. After the NaY was exchanged to NH_4Y and calcined to convert to HY, the product did not carry over the textural properties of the parent NaY and NH_4Y .

Keywords: silica; rice husk; rice husk ash.

INTRODUCTION

Zeolite Y is a type of zeolite in faujasite family and widely known for its use as an adsorbent and as catalyst.¹ It is also commonly used as a catalyst support because of its thermal stability and acidity.^{2,3} Zeolite Y can be synthesized by using various sources of silica (SiO_2). A range of commercial silica sources are available varying from compound, fumed and colloidal forms.³ We previously reported the synthesis of zeolite Y in sodium form (NaY) by using silica from rice husk (RH).⁴ Because of the abundance of rice husk ash (RHA) generated from combustion, it would be worthwhile to compare properties of silica from RH and RHA and the utilization for the NaY synthesis.

RH, generally considered as agricultural waste, is mainly used for energy generation, and also used as raw materials to develop technological products such as high purity silica ash, silicon carbide and zeolites.⁵ A major inorganic component of RH is silica (about 20-30 wt. %).⁶ Upon leaching with mineral acid and calcination, silica with high purity in amorphous form could be extracted from RH.^{4,7} In the past few years our group used rice husk silica (RHS) in the synthesis of different kinds of zeolites including NaY, BEA, MOR, and mesoporous MCM-41.^{4,8}

RHA, derived from burning of RH is also an agricultural excess. RHA is generally used as soil ameliorants to help break up clay soils and improve soil structure but is also used as silica source as an insulator in the steel industry and as a pozzolan in the cement industry. Being less carbonaceous, RHA could be easily processed through heat-treatment to extract amorphous silica.^{6,7} In another couple of studies, RHA containing crystalline tridymite and α -cristobalite was used as an alternative silica source for the syntheses of BEA and ZSM-5 zeolites.⁹ A work characterized the ash produced from combustion of rice husk in fluidized bed reactor showing speed and continuity of the process.¹⁰

The objectives of this paper were to compare the properties of silica from local RH and RHA and the utilization as silica sources for the synthesis of zeolite NaY. The silica and zeolites were characterized by

x-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), and N_2 adsorption-desorption analysis. Moreover, the stability of the zeolite upon transformation to ammonium form (NH_4Y) by ion exchange and to proton form (HY) after a subsequent calcination was also reported.

EXPERIMENTAL

Chemicals and materials

RH and RHA used as raw materials in this work were acquired from a local rice mill and an agricultural store near Suranaree University of Technology, Thailand. The chemicals used for the silica and zeolite NaY synthesis were hydrochloric acid (37% HCl, Merck), sodium aluminate (NaAlO_2 , 50-56% Al_2O_3 , Riedel-de Haen), and sodium hydroxide (97% NaOH anhydrous pellets, Carlo-Erba). The standard zeolite was NaY with a Si/Al molar ratio 5.7 from JRC, Tosoh Corporation, Japan.

Preparation of silica

The extraction of silica from RH was done with a procedure used in our group.⁴ The RH was washed, dried, refluxed with 3 mol L^{-1} HCl at 358 K for 3 h. The resulting RH was then washed until the filtrate was neutral, dried overnight and calcined at 823 K for 6 h to finally produce the rice husk silica (RHS). The same procedure was done on the RHA to extract rice husk ash silica (RHAS) except for the pretreatment washing. RHS and RHAS were dissolved in NaOH solution and filtered to produce sodium silicate (Na_2SiO_3) solution with 28% w/w silica and 11% w/w NaOH.

Synthesis of zeolite NaY

The zeolite NaY was synthesized by using the Na_2SiO_3 solution from RHS and RHAS with a two-step method.⁴ Briefly, a seed gel ($\text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2$) was first prepared by adding Na_2SiO_3 solution into NaAlO_2 solution under stirring until homogenous and left undisturbed

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for 24 h. A feedstock gel ($\text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2$) was also prepared the same way but just before the aging of the seed gel would finish. The seed gel was added into the feedstock gel under high-shear stirring until homogeneous gel was obtained. The overall gel was covered and left to age at room temperature for 24 h before crystallization at 373 K for another 24 h. Finally, zeolite NaY powder was filtered, washed and dried at 373 K.

Transformation of NaY to NH_4Y and HY

Zeolite Y in ammonium form, NH_4Y was prepared by treating the parent NaY in 1 mol L^{-1} NH_4NO_3 solution for 8 h at 353 K and kept for 16 h at room temperature.¹¹ The solution was centrifuged, decanted and the exchange was repeated 3 times. The solids obtained after three ion-exchanges was filtered, washed, and then dried to produce zeolite NH_4Y before it was calcined at 773 K for 3 h to finally produce zeolite in proton form (HY).

Characterization of silica sources and zeolites

The chemical compositions of the prepared RHS and RHAS as well as the synthesized zeolites, calculated as major oxides, were analyzed by EDS (Oxford Instrument ED 2000). The silica and zeolites were carbon-coated before the analysis.

The crystallinity and phase of the silica and the zeolites were determined by XRD (Bruker AXS diffractometer D5005) with nickel-filtered $\text{Cu K}\alpha$ radiation (wavelength = 1.5406 Å).

The textural properties of the zeolites were studied by nitrogen adsorption-desorption analysis using a gas adsorption system (Micromeritics ASAP 2010). The zeolite samples were initially degassed at 573 K under vacuum before the measurements. The analyses were carried out at liquid nitrogen temperature and the specific surface areas were determined from the adsorption data by BET method in the relative pressure range of 0.01–0.30. The micropore sizes were determined by the t-plot method and pore volumes were calculated from the desorption branches of the isotherms using BJH method.

RESULTS AND DISCUSSION

Properties and solubility of RHS and RHAS

After calcination of acid-treated RH, white RHS was produced (Figure 1Sa, supplementary material) with an average yield of 18.07% by weight based on the onset weight of rice husk. The XRD spectrum of RHS (Figure 2S, supplementary material) showed a broad peak at the 2θ value of 22 degrees, a characteristic of silica in amorphous form which is suitable for the preparation of sodium silicate solution necessary for zeolite Y synthesis. Amorphous silica is easily dissolved in basic solution even at room temperature in contrast to crystalline silica.¹² The elemental composition analysis done with EDS showed that the SiO_2 was the only detected component in the extracted RHS. In our previous research, the extracted silica from rice husk consisted of approximately 98% SiO_2 , as analyzed by x-ray fluorescence spectroscopy (XRF).⁴ The chemical composition analysis from XRF also revealed trace amounts of K_2O , Al_2O_3 , CaO and Al_2O_3 but these were not detected by the EDS used in this study. After 6 h of silica dissolution in stirred NaOH solution and subsequent filtration, a clear yellowish viscous sodium silicate solution was produced. Average weight percent recovery of sodium silicate solution after dissolution and filtration was 89.64%.

After the calcination of acid-treated RHA, the RHAS was produced at an average yield of 59.11% by weight. The as-received RHA

samples were black with some gray particles and the resulting RHAS still had black and gray textures after calcination (Figure 1Sb, supplementary material) implying encapsulated carbon residues. Sharp XRD peaks of RHAS at 2θ values of 20.9, 21.9, 26.6, 31.4 and 36.0° indicates silica in crystalline form (Figure 1). These reflections would give corresponding d-values of 4.06, 3.35, 2.85, and 2.49 when used in Bragg's equation. The International Centre for Diffraction Data database reports tridymite (4.06, 3.33, and 10.9) and cristobalite (4.04, 2.49, and 2.84) reflections.¹³ These XRD peaks, therefore, suggest that the RHAS has mixed phases of both forms of crystalline silica. Ashes from long and high temperature pyrolysis of rice husk are known to contain silica in crystalline form and the silica can be dissolved in basic solution at lower rates and higher temperatures in comparison with the amorphous one.^{6,12}

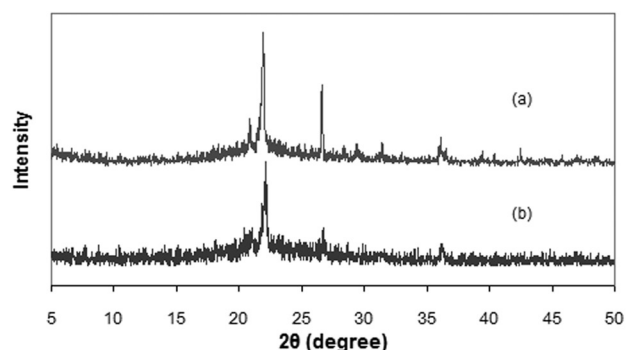


Figure 1. XRD pattern of (a) rice husk ash silica and (b) as-received rice husk ash

At calcination temperatures above 1173 K, the SiO_2 in RHA would consist phases of cristobalite and some tridymite because of the melting of the surfaces of ash silica particles and bonding of particles together.¹⁴ This behavior was demonstrated in the calcination applied here even though the as-received rice husk ash was found to be already in crystalline form according to its XRD spectrum (Figure 1). The as-received RHA only have defined Bragg's peaks at 2θ value of 21.9° and some distinct peaks at 20.9, 26.6 and 36.0°. On the other hand, peaks at 20.9, 26.6, 31.4 and 36.0° were more defined in the XRD spectrum of RHAS compared to that of RHS.

After adding RHAS in stirred NaOH solution, undissolved residue was filtered out indicating poor solubility. The 24-h stirring and dissolution of RHA gave an average percent recovery of sodium silicate solution of only 58.73% by weight while 48-h dissolution gave 76.94% recovery. Despite the relatively low recovery, solution of dissolved silica was nevertheless produced and utilized in the following zeolite synthesis. The level of SiO_2 in RHAS, determined by EDS was 97.56%. Since samples for EDS characterization were coated with carbon before analysis, carbon content of the extracted silica, particularly in RHA, cannot be accounted. Aside from SiO_2 , the RHAS was also found to contain 2.14% K_2O and 0.31% Al_2O_3 . In a study of Della *et al.* using XRF, RHA after calcination at 973 K for 6 h has a SiO_2 composition of 94.95%. Other detections in their study were 0.94% K_2O , 0.90% MgO , 0.74% P_2O_5 , 0.54% CaO and some other traces of oxides.

Synthesis of NaY using RHS and RHAS

Zeolite NaY were synthesized using the Na_2SiO_3 solutions made from RHS and RHAS. The XRD patterns confirmed the characteristic peaks of both zeolite NaY as compared to that of NaY standard (Figure 2), and indicated that the zeolites had long-range structure and

were in pure phase. Both zeolites also had the characteristic peaks of Linde type Y Faujasite published by the International Zeolite Association having strong characteristic reflections at $d = 14.28, 8.75$ and 7.46 \AA .¹⁵ This further suggests that the RHAS was soluble in NaOH solution to some degree even though it was crystalline.

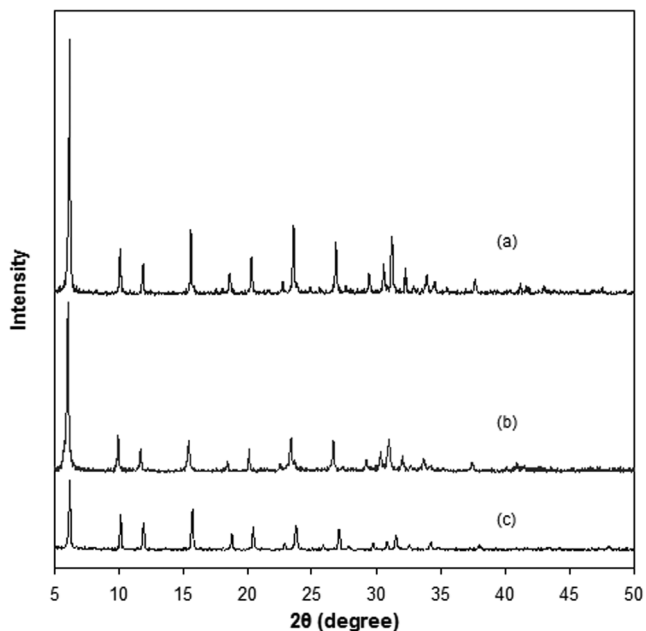


Figure 2. XRD data of zeolite NaY from (a) rice husk and (b) rice husk ash compared with that of (c) standard zeolite NaY (JRC)

When the zeolite NaY synthesized with RHS was analyzed with EDS, it was found to be composed of 63.04% SiO₂, 24.64% Al₂O₃ and 12.28% Na₂O. This would give silicon to aluminum ratio (Si/Al) of 2.26. On the other hand, zeolite NaY from RHAS had a composition of 58.52% SiO₂, 28.14% Al₂O₃ and 13.37% Na₂O. This corresponds to Si/Al equal to 1.84 which, together with that of zeolite from RH, were near the values of 2.43 suggested in the procedure of Ginter *et al.*. Zeolite NaY from RHS was used in the study of zeolite transformation because of its higher crystallinity, aside from the higher silica recovery and simplicity in extraction.¹⁵

Transformation of zeolite NaY to NH₄Y and HY

XRD spectra of NH₄Y after calcination at different conditions are shown in Figure 3. The zeolite lost much of its long-range structure when it was calcined to produce HY at 773 K. No improvement in retaining the structure when the calcination temperature was reduced to 573 K. However, the peaks were more recognizable when the heating rate was decreased to 2 K/min.

On two separate studies, van Bokhoven *et al.* and Xu *et al.* investigated the structural collapse of zeolite Y after subsequent NH₄⁺ ion-exchange and calcination.^{16,17} Both studies attributed the loss of long range structure to the formation of local defects sites in the structure and partial dealumination of the zeolite. Xu *et al.* further explained that the structure collapse of NH₄Y was from the subsequent exposure to moisture in air which changed the coordination number of aluminum atoms in the zeolite from tetrahedral to octahedral even at room temperature.¹⁷ They supposed that when post-calcination HY is exposed to air, a significant fraction of the Al–O bonds are hydrolyzed and broken, leading to a partially amorphous structure and a considerable loss of long-range order and micropore volume.

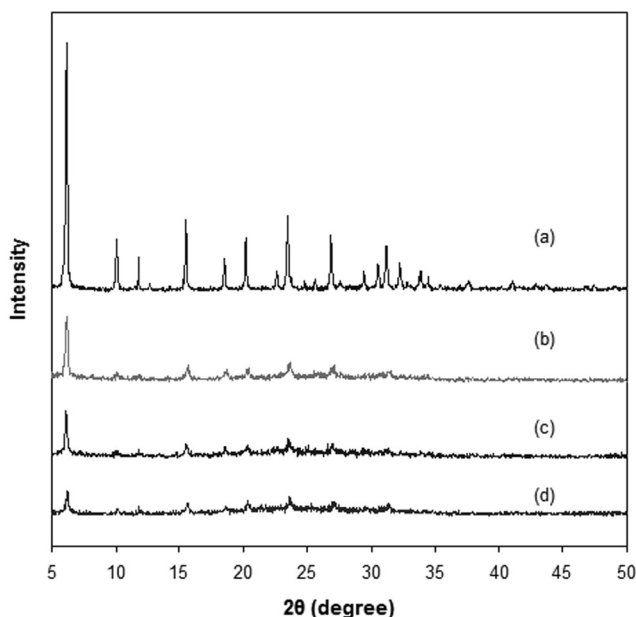


Figure 3. XRD data of (a) zeolite in ammonium form NH₄Y synthesized from rice husk silica, and zeolite NH₄Y calcined at (b) 573 K, heating rate 2 K/min, (c) 573 K, heating rate 5 K/min, and (d) 773 K, heating rate 5 K/min

Table 1. Surface areas and pore volumes of zeolite NaY and HY synthesized from rice husk silica

Properties	NaY	HY
BET surface area (m ² /g)	882	363
Micropore area (m ² /g)	809	222
Micropore volume (cm ³ /g)	0.38	0.11
Average pore size (Å)	22.4	29.0
External surface area (m ² /g)	74	141

Physical properties of the synthesized zeolite NaY and HY are summarized in Table 1. The BET surface areas and micropore volumes were estimated from the N₂ adsorption-desorption isotherms (Figure 3S, supplementary material). The adsorption-desorption isotherms of NaY and HY zeolites exhibited type-I isotherms, characteristic of microporous materials where nitrogen uptake increased quickly at low relative pressure (P/P_0) by adsorption in micropores and external surface. After the monolayer adsorption at low P/P_0 , the nitrogen uptake was almost constant and a small hysteresis loop at high relative pressure was formed in the adsorption-desorption curves. Hysteresis in adsorption-desorption curves suggested some narrow mesopores in the zeolites.¹⁸

The BET surface area of NaY zeolite was 882 m²/g and micropore volume was 0.38 cm³/g. Both are characteristic values for a Y-type zeolite framework. However, the HY did not carry over the textural properties of the parent zeolite NaY and NH₄Y. Slowing down the heating rate on the calcination of NH₄Y from 5 to 2 K/min, although it retained some structure as shown in the XRD spectrum, still diminished much of the surface area (363 m²/g) and micropore volume (0.11 cm³/g). It is also notable that the average pore size (29.0 Å) and external surface area (141 m²/g) of HY were larger than that of NaY.

The zeolite HY was found to be composed of 70.75% SiO₂, 26.17% Al₂O₃ and 3.08% Na₂O which gave Si/Al of 2.39. The Si/Al of HY is close to that of NaY (Si/Al = 2.26) such that the ratio cannot be conclusively identified here as a reason for the difference in thermal stability. Cruciani reviewed factors affecting the thermal stability of zeolites upon heating and observed that the zeolites with

Si/Al ratio of 3.80 or higher are very stable; those with the Si/Al ratio of 1.28 or less are quite unstable; and the stability of those with the intermediate Si/Al ratio are not predictable from the ratio.¹⁹

CONCLUSION

Silica extraction from rice husk (RH) and rice husk ash (RHA) was compared in terms of preparation procedure and yields. Although both are good alternative sources of silica, RH is the better source than RHA for zeolite NaY synthesis taking into account the efficiency in product recovery and simplicity of extraction. Silica from RH was amorphous whereas that from RHA contained crystalline tridymite and cristobalite. Silica extracted from RH was found to contain exclusively SiO₂ while silica from RHA has 97.56% SiO₂ with traces of K₂O (2.14%) and Al₂O₃ (0.31%). Zeolite NaY showed relatively large BET surface area of 882 m²/g and micropore volume of 0.38 cm³/g, both are characteristic values for a Y-type zeolite framework. However, HY did not carry over the textural properties of the parent zeolite NaY and NH₄Y because of the structure collapse resulting from the change of aluminum coordination in the structure after the calcination.

SUPPLEMENTARY MATERIAL

Available at <http://quimicanova.sbg.org.br>, in format PDF, with free access.

ACKNOWLEDGMENT

This research was supported by Suranaree University of Technology (SUT).

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