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ORIGINAL ARTICLE

Rice husk ash as a renewable source for the production of zeolite NaY and its characterization

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Abstract Zeolite Y in sodium form (NaY) was synthesized using silica source from rice husk. The as-synthesized samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray fluorescence (XRF), BET. As results, we verify that NaY zeolite obtained from the two-step route, presents a good degree of crystallinity and then can be suitable for using in various applications.

1. Introduction

Silica is the most abundant oxide in the earth's crust, yet despite this abundance, silica is predominantly made by synthetic means for its use in technological applications and it is one of the valuable inorganic multipurpose chemical compounds (Londeree et al., 2002). Naturally occurring silica, especially those found in agro waste, can provide an alternative source to replace commercial silica precursors. Rice husk saw dust (Venkat and Vijay Babu, 2011), and rapeseed stalk (Seung et al., 2011) are among the widely studied agro wastes which have been converted into more valuable end products.

Rice husk (RH) is therefore an agricultural residue abundantly available in rice producing countries. Much of the husk produced from the processing of rice is either burnt or dumped as waste. Even though some of this husk is converted into end products such as feedstock (Maiti et al., 2006) and adsorbent (Hyun et al., 2009) most is burnt openly, causing environmental and health problems especially in poor and developing countries. Therefore, it is very important to find pathways to fully utilize the rice husk. Silica can be pyrolyzed at elevated temperatures to form rice husk ash (RHA) or it can be extracted from rice husk in the form of sodium silicate by using a solvent extraction method. In most applications, rice husk ash is more favorable compared to rice husk. Rice husk ash is a general term describing all forms of the ash produced from burning rice husk. It would be beneficial to the environment to recycle the waste to produce eco-material having a high end value (Pijarn et al., 2010).

Nowadays, zeolites as well as the other molecular sieves find several application in a diverse areas. In particular, zeolites are hydrated, crystalline aluminosilicates constructed from TO_4 tetrahedra (T = Al, Si) where each apical oxygen

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atom is shared with an adjacent tetrahedron. Zeolite Y is a highly versatile molecular sieve from the faujasite family of zeolites whose 7.4 Å, three-dimensional pore structure and solid acidity make it useful as a catalyst, ion exchanger, adsorbent, etc. Zeolite Y is commonly prepared with a high aluminum content, but in most cases it is employed in a silicon-enriched form.

The objective of this paper is to explore the synthesis of zeolite from RHA as a source of silica after extraction in the amorphous form by acid leaching of husks. Two different synthetic routes one-step and two-step, and crystallization time were applied. Also, characterizations of RHA were investigated including; chemical analysis, XRD and SEM. The physical properties and crystallinity of the synthesized zeolites are discussed based on the results obtained by means of various spectroscopic techniques including XRD, N_2 adsorption and SEM.

2. Experimental

2.1. Materials

White RHA obtained from a rice field in Egypt contained 94 wt.% SiO_2, 0.19 wt.% Al_2O_3, 0.32 wt.% CaO and 1.64 wt.% K_2O. Other materials used were; hydrochloric acid (37 wt.% HCl Merck), sodium aluminate (54 wt.% Al_2O_3: 41 wt.% Na_2O technical grade), sodium hydroxide (97 wt.% NaOH, Carlo-Erba), and potassium hydroxide (85 wt.% KOH, Sigma Aldrich). Standard zeolites were NaY with Si/Al molar ratio 5.7 (JRC with Tosoh Crop) and NaP (Fluka).

2.2. Silica extraction

Initially, adhered dirt and soil on RH can be removed by washing with plenty of tap water and rinsing with distilled water. The metallic impurities in RH can be reduced to negligible levels by refluxing with hydrochloric acid (Chang et al., 2006). Direct extraction of silica can be performed by stirring the acid treated RH (after drying) with sodium hydroxide solution. During this process, silica is extracted in the form of sodium silicate together with other organic moieties, according to the method patented by Adam and Fua (Adam, 2008). The sodium silicate obtained is converted to silica by adding suitable amounts of mineral acid. Rice husk ash (RHA) can be obtained by pyrolyzing the RH at temperatures ranging from 500 °C to 800 °C for 5–6 h in a muffle furnace (Carbolite) to remove the organic contents. The yield of silica in this sample ash was 89.00%. Chandrasekhar et al., (2006) studied critically the effect of acid treatment, calcination temperature and the rate of heating of RH and showed that these parameters influenced the surface area, reactivity toward lime and brightness of the ash. The obtained chemical compositions of rice husk ash are tabulated in Table 1. Also, the whole experimental process is shown in Fig. 1.

Table 1 Chemical composition of RHA determined by XRF.

Chemical compositions of RHA	Wt.%
SiO_2	89.00
Al_2O_3	1.20
Fe_2O_3	1.28
K_2O	1.22
CaO	1.00
C	18.24

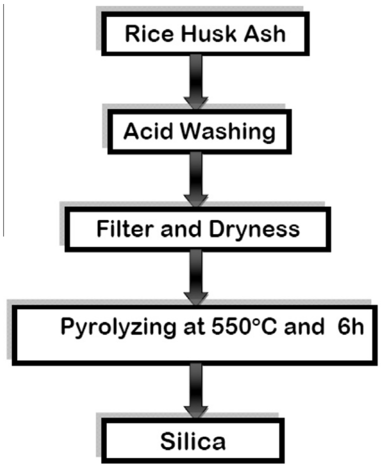

Figure 1 Flow diagram of the procedure was used to extract silica powders from RHA.

2.3. Synthesis of zeolite NaY

NaY zeolite was synthesized as shown in Fig. 2. Shortly, the seed gel (Al_2O_3:10SiO_2) was prepared first by adding the Na_2SiO_3 solution prepared from RHA into sodium aluminate solution under stirring until homogenous and left undisturbed for 24 h at room temperature. The feedstock gel (Al_2O_3:10SiO_2) was also prepared in the same way just as it was used immediately without aging.

The seed gel was then mixed into the feedstock gel under vigorous stirring until a homogeneous gel was obtained. The resulting overall gel is divided into two portions (G_1 and G_2); G_1 was covered, left to age at ambient temperature for 24 h, and crystallized at 110 °C for another 24 h (two-step route); the final obtained product, was filtered, washed, and dried at 100 °C in an oven. G_2 was crystallized by autoclave directly for 110 °C for 24 h (one-step route), then the final product, was filtered, washed thoroughly with distilled water, and dried at 110 °C.

2.4. Experimental techniques

2.4.1. X-ray fluorescence

Chemical composition of rice husk ash was examined by X-ray fluorescence spectroscopy (XRF: Philips, PW1400).

2.4.2. N_2 adsorption

The specific surface areas (BET), pore volumes, and pore sizes of NaY were determined by a Quantachrome (NOVA 2000) 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.

2.4.3. X-ray diffraction analysis

X-ray diffractograms of RHS and the synthesized NaY were measured by a Bruker axis D_8 diffractometers. The patterns

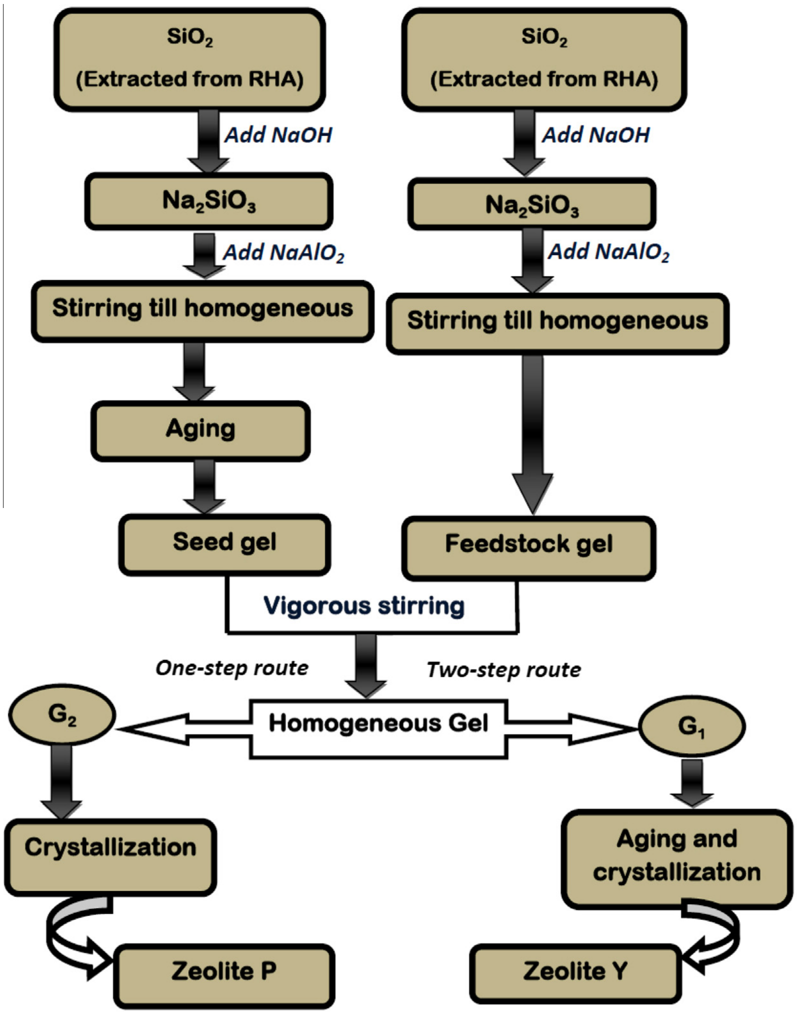

Figure 2 Flow diagram of the procedure was used to prepare zeolite Y and zeolite P.

were run with Cu Kα radiation (Kα = 1.540 Å). The average crystallite size of the powders was estimated automatically from corresponding XRD data using the Scherrer formula.

2.4.4. Scanning electron microscopy

The morphology and habit of the crystalline phase of the products were examined on a scanning electron microscope SEM (JEOL JSM-6400) with an applied potential of 10 kV.

2.4.5. Particle size distribution

Particle size distribution was determined by Dynamic light scattering, LB-500.

3. Results and discussion

3.1. Characterization of RHA

3.1.1. The composition analysis of RHA

The composition of minerals leached from RHA was shown in Table 1. The gross weight of silicon dioxide in the RHA was 89.00 wt.%, and the residual was carbon and other impurities. The conclusion is that preliminary leaching of rice husks with a solution of HCl, boiled before thermal treatment has been proved (Real et al., 1996; Krishnarao et al., 2001; Chen and Chang, 1991) to be an effective way in substantially removing most of the metallic impurities and producing RHS completely white in color. In addition, 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 rice husk combustion without leaching (Sun and Gong, 2001).

3.1.2. XRD analysis

The micrograph shows the aggregates of particles in RHS. Besides that, the diffractograms reveal that RHS is amorphous (Fig. 3). It was observed that, only a broad peak with 2θ at 22 degree, is a characteristic of amorphous silica. Alongside, this form of silica is suitable for zeolite synthesis because it dissolves easily in NaOH solution to form sodium silicate.

3.1.3. Scanning electron microscopy analysis

From the SEM image of silica in Fig. 4, amorphous shape, which is a characteristic of amorphous silica, was observed.

3.2. Characterization of zeolite Y

3.2.1. X-ray diffraction

In the present work, one deals with two synthetic routes for NaY synthesis. The products from both routes were

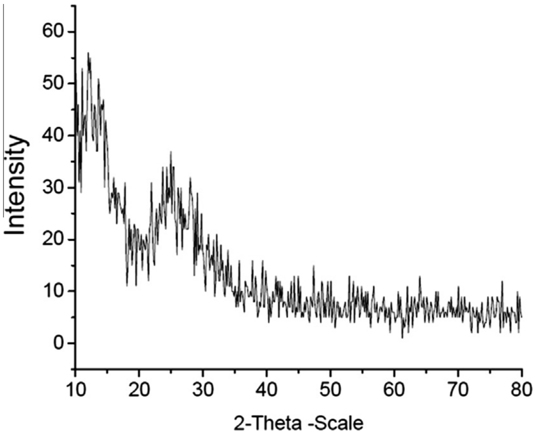

Figure 3 XRD pattern of silica from RHS.

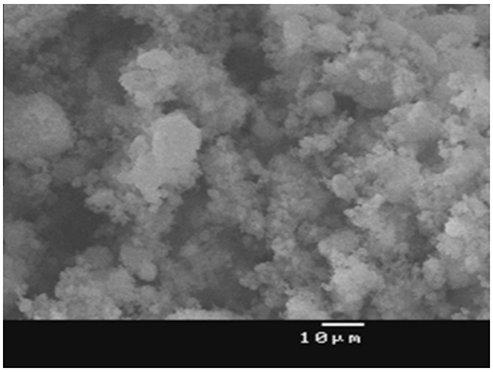

Figure 4 SEM image for silica from RHS.

characterized by XRD compared with the patterns pertaining to standard NaY. Fig. 5, illustrates the XRD patterns of the synthesized NaY (two-step route), comparing with those of the standard NaY; one could reveal that there is no difference between peaks which means that the product from the two-step route contained NaY in the pure phase. On the contrary, the characteristic peaks pertaining to the product from the one-step route (NaP) are different from those of the standard NaY. It was reported that aging time was essential for the synthesis of NaY (with Si/Al ratio 1.8) from kaolin (Chandrasekhar and Pramada, 2004). 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 the pure 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 the 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 (Oh et al., 2001).

3.2.2. Study of crystallization time in two-step route

It was mentioned before, that in the synthesis of NaY by the two-step route, the crystallization time varied from 12 to

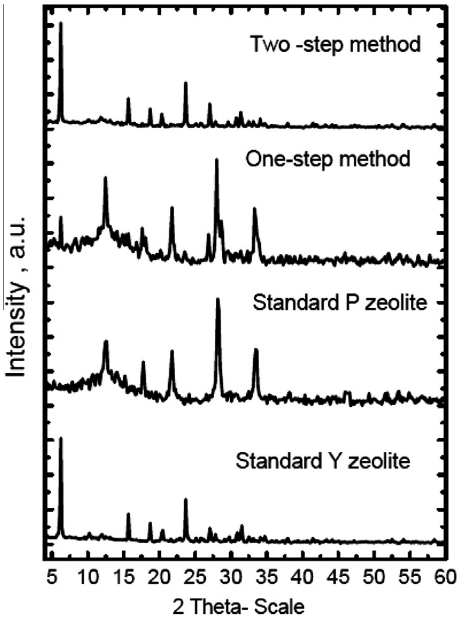

Figure 5 XRD pattern of the prepared samples from one-step and two-step syntheses, standard Y zeolite and standard P zeolite.

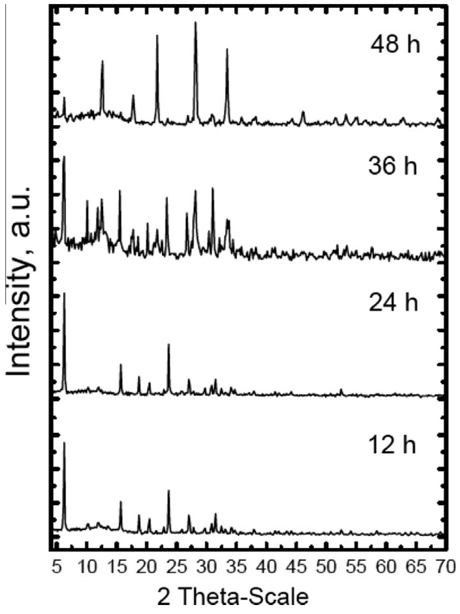

Figure 6 XRD pattern for two-step synthesis crystallized at different crystallization times.

Table 2 Textural properties of synthesized samples from one- and two-step routes.

Samples	S_{BET} (m^2/g)	Vp (cm^3/g)
One-step	406.6	0.190
Two-step		
12 h	528.5	0.240
24 h	716.6	0.350
36 h	32.5	0.006
48 h	18.6	0.002

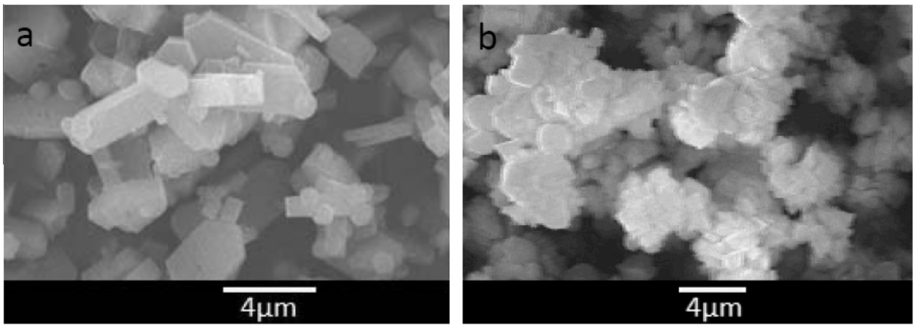

Figure 7 SEM images for prepared samples by two-step route crystallized at 24 h (a) and 48 h (b).

48 h. The spectrum showing this variation of crystallization time pertaining to NaY displayed in Fig. 6 (A and B, respectively), reveals that at a crystallization time of 24 h zeolite Y shows a higher intensity compared to a crystallization time of 12 h. Moreover, the relative crystallinity of NaY at 12 h was approximately 65% compared to that at 24 h. After 24 h, additional peaks in XRD spectrum, which are characteristic of zeolite NaP appeared. The intensity of NaP peaks increased with crystallization time, while that of the peaks of NaY decreased. At 36 and 48 h the main peak corresponding to NaY was not observed and the peaks of NaP were dominant (Fig. 6, spectrum C and D) indicating that the optimum crystallization time for the synthesis of zeolite NaY with RHS was 24 h.

3.2.3. Surface texture

The different surface characteristics of various investigated zeolites were determined from N_2 adsorption isotherms conducted at 77 K. Inspection of Table 2 reveals the following:

(i) 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 as in Fig. 6 as mentioned above.
(ii) The product from a crystallization time of 24 h had a surface area of 716.6 m^2/g, which was higher than that obtained from a crystallization time of 12 h that was 528.5 m^2/g, this is evidence that crystallization for 24 h allowed a more complete formation of NaY.
(iii) The surface area of the products from a crystallization time of 36 and 48 h was much lower because the major products were zeolite P, which was a less porous phase.

3.2.4. Morphology of NaY by SEM

Fig. 7(a) shows the morphology of NaY (two-step route and 24 h crystallization time) and displays the particles of NaY which were uniform in size and also; some crystals apparently fused together forming agglomerate particles. Moreover, the particle size of isolated crystals from SEM micrograph was approximately 4 μm. As mentioned earlier, the main peak of NaY disappeared completely and the major transformation product after crystallization for 48 h was NaP. The morphology of NaP is shown in Fig. 7(b), the crystal shape of NaP was apparently different from that of NaY Fig. 7(a). The shape of NaP crystals could not be confirmed by SEM micrograph because most crystals had been cracked through the center.

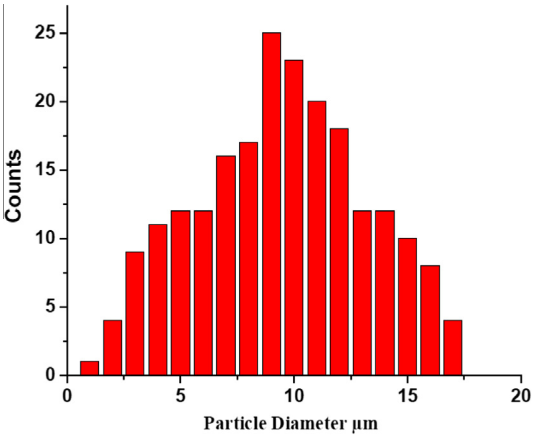

Figure 8 Histogram of diameter distribution of zeolite Y synthesized from RHS after 24 h of crystallization.

3.2.5. Particle size distribution of NaY

Histogram of the diameter distribution of zeolite Y after 24 h of crystallization time is displayed in Fig. 8. The results revealed that the average particle size was approximately 10 μm. It was observed that this obtained value was different from the size of isolated crystals from SEM because several crystals fused together forming large particles; which is evidence that zeolite particles are showing homogeneity.

4. Conclusions

The rice husk ash is well employed in the synthesis of zeolite particles (NaY and NaP). Physicochemical properties of the produced zeolite, after optimizing the various synthesis conditions (24 h of crystallization time and 110 °C) were characterized. The NaY zeolite synthesized has a uniform distribution of particle size that SEM shows. The obtained data from particle size distribution showed homogeneity of zeolite Y. BET results revealed that, 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. In the two-step route, a 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 zeolite P. The optimum crystallization time for the synthesis of zeolite NaY with RHS was 24 h.

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