Ultrasonic and conventional synthesis of NaA zeolite from rice husk ash

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Abstract. In the present work, a simple synthetic route for the production of single phase NaA zeolite is demonstrated. Rice husk ash (RHA) as alternative silica source was employed for the synthesis by conventional hydrothermal and non-conventional ultrasound methods. The zeolite was also synthesized using commercially available silicate for comparison. The effect of the reaction time (2, 4 and 6 h) at a fixed temperature of 70°C was investigated. The elemental, structural and morphological characterization of the ashes and the synthesized zeolites was performed by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and thermogravimetric analysis (TG/DSC).

1. Introduction

Zeolites are crystalline microporous aluminosilicates which are constructed from tetrahedral AlO4 and SiO4 units. The porous structure of zeolites yields valuable physicochemical properties for cation exchange, molecular sieving, catalysis and adsorption whereby this are good candidates for a large number of applications. The search for new materials with improved properties for different applications has motivated the research in the synthesis of zeolites and related materials since some decades and today continues to be a topic very addressed in the scientific literature. Conventionally zeolites are synthesized under hydrothermal conditions, and the reaction gel medium contains the framework atoms, solvents, structure-directing agents (SDAs) and mineralizers.

Ultrasound is a new method for the synthesis of a wide range of nano- and micro-particles. It is very simple, fast and does not need any complicated facilities. This technique has also been introduced in the field of zeolite synthesis. In a recent review Askari et al. summarized the effects of ultrasound on the synthesis of various zeolites. The most important mechanism enhancing crystallization is ultrasonic cavitation, a phenomenon that can be defined as the growth and explosive collapse of microscopic bubbles. The use of ultrasonic treatment in synthesis reactions offers several practical
advantages among which the lower-temperature and the shorter time required for the synthesis process are the most significant.

Rice husk (RH) is an agricultural waste material abundantly available in rice-producing countries. It is known that rice husk ash (RHA) usually contains over 80% of silica, reason why it has been investigated as an alternative source of silica for different applications. For example RHA has been widely used as additive for construction material and as an adsorbent for organic dyes and inorganic metals. RHA can also be an economically raw material for the production of zeolites. Several researchers have been report the synthesis of zeolites ZSM-5, ZSM-11, Beta, EMT, Y, mordenite, NaA and NaX starting from RHA. However, only few papers combined the use of RHA as silica source and the ultrasound energy for the synthesis of zeolites.

The present work aims to evaluate the applicability of ultrasound method to the synthesis of Na-LTA zeolite using a low cost, abundant and renewable source of amorphous silica extracted from a waste of the Cuban agricultural industry, the rice husk. Furthermore, the characterization of the obtained materials is carried out in order to evaluate its potential in later applications.

2. Experimental

2.1. Rice husk ashes

Rice husk of national production was kindly provided by the Research Institute of Grain of Cuba. It was washed with distilled water to remove dust and mud and calcined at 500 and 700 °C for 2 hours in a muffle to obtain rice husk ashes (RHA-500 and RHA-700, respectively). The chemical compositions of the RHAs obtained, expressed in weigh %, are shown in Table 1.

|     | SiO₂ | C  | Na₂O | K₂O | CaO | MgO | MnO | Al₂O₃ | P₂O₅ |
|-----|------|----|------|-----|-----|-----|-----|-------|------|
| RHA-500 | 81.4 | 6.4 | 1.9  | 3.6 | 1.0 | 1.5 | 0.9 | 1.2   | 2.0  |
| RHA-700 | 92.5 | -- | 0.5  | 2.1 | 1.0 | 1.0 | 0.9 | 0.9   | 1.1  |

To optimize the extraction of silicon from the ash a known amount of RHA-700 was mixed with a 2 M NaOH solution at a solid/liquid ratio of 1 g / 10 ml and was left under vigorous stirring for different times at 55 °C. Then, the solution was separated from the mixture by centrifugation and the solid residues were washed with distilled water and dry until constant weight.

2.2. Synthesis of zeolites

For the zeolite synthesis the following composition of the initial gel was selected: 3.5Na₂O: Al₂O₃: 2SiO₂: 145H₂O. Such composition is typically employed for LTA zeolite synthesis, although other reports can be found in the literature with different contents of water and Na₂O.

Two different series (SI and SII) were synthesized starting from RHA and commercial sodium silicate, respectively. The sodium silicate solution for SI was prepared mixing 1 g of RHA-700 with 10 ml of 2 M NaOH solution followed by vigorous stirring for 4 h at 55 °C. Then the solution was left to cool and solid residue was separated by centrifugation. The sodium silicate solution for SII was prepared dissolving 3.14 g of Na₂SiO₃·5H₂O in 8.67 ml of H₂O. A clear aluminate solution was prepared by mixing 1.75 g of sodium aluminate with 4 ml of 2 M NaOH solution and 5 ml of H₂O followed by stirring at room temperature until complete dissolution. The silicate solution was added slowly into the aluminate solution while stirring vigorously and then the obtained gels were heating at 70 °C for different times (2, 4 and 6 h) in a conventional ultrasonic bath and in an oven under static conditions. After the crystallization time, the solids were separated by centrifugation, washed repeatedly with distilled water, dried at 70 °C and stored for further characterization. For the ultrasonic
synthesis a commercial ultrasonic cleaner (VWR) with a frequency of 35 kHz and temperature control was employed. The samples were labelled as SI-HT-t and SI-US-t for samples of SI series and SII-HT-t and SII-US-t for samples of SII series obtained by hydrothermal and ultrasound methods, respectively, where t correspond to the crystallization time.

2.3. Characterization techniques
The characterization of the RHAs and the synthesized zeolites was performed by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and thermogravimetric analysis (TG/DSC). For qualitative XRD analysis a Philips Xpert diffractometer was employed, using Cu Kα radiation ($\lambda = 1.541838$ Å). The 2$\theta$ range from 1° to 60° was swept in a continuous way at 2 °min$^{-1}$. The morphologies of the samples and chemical analysis were investigated by SEM and EDS on a JEOL 5600 microscope. TG/DSC analysis was carried out with the aid of a NETZSCH STA 409 PC/PG thermal analyzer. Samples were heated form 25 to 800 °C at a heating rate of 10 °C/min under dry air at a purging flow rate of 50 mL/min. The sensitivity of the thermobalance was ± 1 μg. A solid sample of about 15 mg was used in each test.

3. Results and Discussion

4. Rice husk ashes
RH calcined at both temperatures (500 and 700 °C) produces amorphous silica as is evident from a broad hump at the 2$\theta$ of around 15–30° in the X-ray diffraction patterns (Figure 1). This result is very suitable for further synthesis because the silica is rendered active in its amorphous form to produce zeolites. Similar results have been reported by other authors for calcinations temperatures smaller than 700 °C for short times. However, for higher temperatures or larger times crystalline phases of SiO$_2$ such as cristobalite, tridymite and α-quartz are obtained.

Figure 2 shows the results of the thermogravimetric analysis of RH and RHA ashes. RH undergoes a total mass loss of about 85 % that occurs in three steps, at 78, 292 and 470 °C. The first loss of mass is related to the loss of water and the two others with the decomposition of the organic matter (mainly cellulose, hemicellulose and lignin). The total loss of mass for RHA-500 and RHA-700 is of 5 and 1 %, respectively. In RHA-700 this loss of mass corresponds to the loss of water while in RHA-500 is due to the decomposition of organic matter. Taking into account the content of SiO$_2$ and that the unburned organic matter could interfere in the subsequent synthesis of the zeolite, we selected as silica source the ash obtained at 700 °C.
by rice husk calcination at 500 and 700 °C. (A) and rice husk ashes (B).

Figure 3 shows the percent of silicon extracted from RHA-700 in function of the time using a 2M NaOH solution at 55 °C. The amount of silicon extracted increased with the increasing of time. However, no significant increase was observed at longer extraction time than 4 h. It was found that in these conditions is possible to extract about 90% of the content of silicon present in the ash, so that we select 4 hours as optimum extraction time.

![Figure 3. Percent of silicon extracted from RHA-700 in function of time employing a 2M NaOH solution at 55 °C.](image)

5. Characterization of the synthesized zeolites

The XRD patterns of the synthesized zeolites are shown in Figures 4 and 5. The diffractograms of all the samples matched the reference peaks of NaA zeolite (PDF: 01-089-8015) and no others zeolitic phases appear, which ascertain the successful synthesis of high purity NaA zeolitic phase. It can be noted that RHA-700 is a suitable silica source for the synthesis of NaA. For both methods it was possible to synthesize the desired zeolite to a moderate temperature, short crystallization time and without seeding and aging.

![Figure 4. XRD patterns of NaA zeolites synthesized from RHA-700 as silica source by hydrothermal and ultrasound methods for different times.](image)
The comparison of the diffraction patterns allows affirming that for both methods a larger crystallization time is needed for SI series (samples obtained starting from the ash), which could be related with the presence of impurities in the extracted silica. Also, for both series the crystallinity of zeolite A started to develop at earlier synthesis times, indicating an increase in the nucleation rates in the presence of ultrasound. These statements are better illustrated in Figure 6, where the degree of crystallinity in function of the crystallization time is presented. The crystallinity was calculated as the sum of the intensities of the representative diffraction planes of NaA, normalized by assuming that this sum for SII-HT-6 corresponds to 100 % of crystallinity. Park et al. found similar results when they studied the conventional and ultrasound synthesis of zeolite 4A from kaolin at 60 and 70 °C. Andaç et al. reported that nucleation and crystallization rates, as well as the yield of zeolite A increased as a result of the application of ultrasound.

The SEM images of the zeolites are shown in Figure 7. A uniform particles morphology -cubic of smoothed edge- can be observed, which are characteristics of zeolite A. Contrary to other works not significant differences in the particle size were observed for hydrothermal and ultrasound methods. It is interesting to note that as early as 2 hours for the ultrasonic synthesis of the SII series a large number of crystals appears.
The chemical composition of the samples (determined by EDS) are presented in Table 2. The calculated Si/Al ratios are around 1. Among the metals found as traces in the ash only the potassium is involved in the synthesis of the zeolite, appearing in very small amounts in the final chemical composition.
Table 2. Chemical composition of the synthesized zeolites determined by EDS. The values are expressed in wt. %.

| Sample   | Si   | Al   | O    | Na   | K    | Si/Al |
|----------|------|------|------|------|------|-------|
| SI-HT-2  | 12.65| 12.55| 62.83| 11.64| 0.29 | 1.007 |
| SI-HT-4  | 12.44| 12.47| 62.89| 11.88| 0.31 | 0.998 |
| SI-HT-6  | 11.67| 12.04| 64.57| 11.50| 0.17 | 0.969 |
| SI-US-2  | 13.16| 13.27| 62.12| 11.09| 0.35 | 0.992 |
| SI-US-4  | 12.24| 12.39| 62.98| 12.12| 0.25 | 0.988 |
| SI-US-6  | 11.80| 12.29| 64.26| 11.47| 0.16 | 0.960 |
| SII-HT-2 | 12.24| 12.39| 62.05| 13.26| 0.01 | 0.988 |
| SII-HT-4 | 12.08| 12.40| 64.03| 11.46| 0.00 | 0.974 |
| SII-HT-6 | 11.58| 11.94| 65.05| 11.41| 0.01 | 0.970 |
| SII-US-2 | 12.26| 12.51| 62.73| 12.48| 0.01 | 0.980 |
| SII-US-4 | 10.84| 11.34| 66.79| 10.98| 0.03 | 0.956 |
| SII-US-6 | 11.18| 11.63| 65.75| 11.41| 0.02 | 0.961 |

The DTG curves of the samples of SI and SII series are given in Figure 8 and 9, respectively. It can be observed that the curves for the amorphous samples were quite different than those of the crystalline and partly crystalline samples. In all curves there are a minimum at about 95 °C, which corresponds to the removal of moisture. The intensity of this temperature minimum was higher for the amorphous sample and decreases with the increases of crystallinity. For samples of higher crystallinity the DTG curves exhibited others two minimums at around 170 and 410 °C, which have been related with the loss of water molecules coordinated to the Na ions and inside the sodalite cage cavities, respectively.

![Figure 8. DTG curves of zeolites obtained from RHA-700 (SI series) by hydrothermal (A) and ultrasound (B) methods.](image1)

![Figure 9. DTG curves of zeolites obtained from sodium silicate (SII series) by hydrothermal (A) and ultrasound (B) methods.](image2)

6. Conclusions

It was verified that it is feasible to use the silicon extracted from rice husk ash as starting material for the synthesis of NaA zeolite with good purity, suitable morphology and with a Si/Al ratio close to 1. The results show that the ultrasound synthesis favors the kinetics of the reaction, yielding more crystalline samples in less time.
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