

LOW COST SYNTHESIS AND CHARACTERIZATION OF ZEOLITES FROM SILICON NATURAL SOURCES FOR ENVIRONMENTAL APPLICATIONS

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ABSTRACT

The synthesis of hierarchical zeolites for their future environmental application in the removal of heavy metals and pharmaceuticals is presented. A low cost, abundant and renewable amorphous silica extracted from a waste of the Cuban agricultural industry, the rice husk, was employed as alternative silicon source for the synthesis. The effect of Si/Al ratio, aging time, used template and time and temperature of reaction, on the structural characteristics of the obtained material was investigated. The elemental, structural and morphological characterization of the ash and the zeolites was performed by XRD, SEM, EDS and TG. The SEM images of zeolites synthesized with Si/Al = 1 (serie I) show a uniform morphology -cubic of smoothed edge- characteristics of zeolite A, with mean particle size of about 0.5 μm . The diffraction patterns of the samples matched the reference peaks of NaA zeolite. The zeolites synthesized with Si/Al = 2 (serie II) have an octahedral morphology characteristic of the faujasite phase, with particle sizes of about 1 μm , and the diffraction patterns matched with that reported for X zeolite. The increase of the aging time and surfactant concentration slightly decrease the particle size, which is evidenced in the increase of the half-width of the diffraction peaks. The global results demonstrated that it is possible to synthesize A and X zeolites at moderate temperatures, short crystallization times, without seeding, and with a good purity starting from rice husk ash as silicon source.

Keywords: zeolite synthesis, hierarchical zeolites, A zeolite, X zeolite, rice husk ash.

SÍNTESIS Y CARACTERIZACIÓN DE ZEOLITAS JERARQUIZADAS A PARTIR DE FUENTES NATURALES DE SILICIO PARA APLICACIONES AMBIENTALES

RESUMEN

Se presenta la síntesis de zeolitas jerarquizadas para su futura aplicación ambiental en la eliminación de metales pesados y productos farmacéuticos. Una sílice amorfa de bajo costo, abundante y renovable, extraída de un residuo de la agroindustria cubana, la cáscara de arroz, fue empleada como fuente alternativa de silicio para la síntesis. Se investigó el efecto de la relación Si/Al, tiempo de envejecimiento, plantilla utilizada y tiempo y temperatura de reacción, en las características estructurales del material obtenido. La caracterización elemental, estructural y morfológica de la ceniza y las zeolitas fue realizada por XRD, SEM, EDS y TG. Las imágenes SEM de las zeolitas sintetizadas con Si/Al = 1 (serie I) muestran una morfología uniforme -cubo de bordes alisados- característica de la zeolita A, con tamaño de partícula promedio de alrededor de 0.5 μm . Los patrones de difracción de las muestras coinciden con los picos de referencia de la zeolita NaA. Las zeolitas sintetizadas con Si/Al = 2 (serie II) tienen una morfología octaédrica característica de la fase faujasita, con tamaños de partícula de aproximadamente 1 μm , y los patrones de difracción coinciden con los reportados para la zeolita X. El aumento del tiempo de envejecimiento y la concentración de surfactante disminuyen ligeramente el tamaño de partícula, lo que se evidencia en el aumento del semiancho de los picos de difracción. Los resultados globales demostraron que es posible sintetizar zeolitas A y X a temperaturas moderadas, cortos tiempos de cristalización, sin siembra y con una buena pureza, a partir de ceniza de cáscara de arroz como fuente de silicio.

Palabras claves: síntesis de zeolitas, zeolitas jerarquizadas, zeolita A, zeolita X, ceniza de cáscara de arroz.

INTRODUCTION

Growing industrialization has caused an increase in the exploitation of water resources, affecting negatively its quality. For this reason, the scientific community is looking for more efficient and economic technologies for their remediation. The use of natural zeolites distinguishes between these methods due to their low cost, excellent properties as ion-exchanger and adsorbent, as well as good thermal and chemical stability [1, 2]. Zeolites has been used for the adsorption of a wide variety of organic compounds in water, such as: pesticides, dyes, and drugs, as well as for the removal of NH_4^+ , heavy metals and radionuclides [3, 4].

Although Cuba has large zeolitic deposits, in some cases is more efficient the employment of synthetics zeolites, which can be designed specifically for the desired application. The presence of only micropores in zeolitic materials limits their applications in the adsorption of bulky molecules due to diffusion restrictions. In order to minimize such restrictions, numerous methods have been developed in the last years to introduce mesoporosity in zeolitic materials, or zeolitic crystalline character in mesoporous materials [5, 6]. Nanozeolites with a high proportion of external surface area accessible to bulky molecules, mesoporous zeolites or zeolitic-mesoporous hybrid materials with crystalline walls formed by zeolitic structures have been reported [7-9]. They all have interesting textural properties for their application in reactions involving bulky molecules and can be referred to as zeolite materials with hierarchical porosity, since they have at least two types of pore systems with sizes included in different ranges.

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, consequently it has been investigated as an alternative source of silica for different applications. For

example RHA has been used as an adsorbent for organic dyes [10] and inorganic metals [11, 12] and as raw material for the synthesis of zeolites. For example the synthesis of ZSM-5 [13, 14], ZSM-11 [15], Beta [16], EMT [17], Y [18], mordenite [19], NaA [20-23] and NaX [23] zeolites starting from RHA has been reported.

In this work, we present the results of the synthesis and characterization of zeolites prepared by hydrothermal conventional methods, starting from rice husk ash as silicon source, for their future application in environmental remediation as the removal of heavy metals and pharmaceuticals. We used cationic surfactants during the zeolites synthesis as templates for the creation of a mesoporous system, although the characterization necessary to ensure their formation is still under development and it will be published in later works.

MATERIALS AND METHODS

Rice husk ash (RHA) was prepared employing the method reported by Ledesma et al. [24]. Rice husk (kindly supply by the Cuban Research Institute of Grain) was washed with water to remove dust and mud. Then acid washes were performed with HCl 1 M to remove impurities including iron, calcium, magnesium, sodium and potassium. Finally, washed rice husk was calcined at 700 °C for 2 hours in a muffle to obtain rice husk ash (RHA). Sodium silicate solution was prepared by mixing 1g of the ash with 10 mL of 2 M NaOH solution and stirring for 4 hours at 60 °C [22]. A clear aluminate solution was prepared by mixing a known amount of sodium aluminate with 2 M NaOH solution and H_2O , followed by stirring at room temperature until complete dissolution. For zeolite synthesis two composition of the initial gel were employed (serie I: $3.5\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 2\text{SiO}_2 : 145\text{H}_2\text{O}$ and serie II: $3.5\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 4\text{SiO}_2 : 145\text{H}_2\text{O}$). Such compositions are typically employed for

LTA zeolite synthesis [25], although other reports can be found in the literature with different contents of water and Na₂O. Benzyl dimethyl alkyl ammonium chloride surfactants with different chain length (12, 14 and 16 carbon atoms) were used as template for create mesoporosity, at a final concentration in the gel of 2 and 4 times their critical micellar concentration values (CMC). The sodium silicate solution was dropped into the sodium aluminate solution while stirring vigorously. The desired amount of surfactant was added to the gel, stirred and aging for 6, 12 and 20 days at room temperature. The aging gels were annealing at 70 °C for 6 hours for serie I and 90 °C for 12 hours for serie II, in a conventional 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. Fig. 1 shows a schematic representation of the synthesis method.

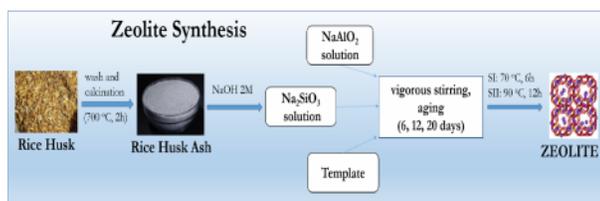


Fig. 1. Schematic representation of the zeolite synthesis.

For qualitative XRD analysis a Philips Xpert diffractometer was employed, using Cu K α radiation ($\lambda = 1.541838 \text{ \AA}$). The 2θ range from 1° to 60° was swept in a continuous way at 2° min^{-1} . The morphology of the samples and chemical analysis were investigated by SEM and EDS on a TESCAM microscope equipped with an OXFORD Electronic Probe. The SEM particle size data was fitted assuming a normal probability density function (Eq. 1), where D_m is the mean particle size and σ is the standard deviation used to quantify the variation or dispersion of the particle size. The statistical analysis was

based on a count of approximately 100 individual nanoparticles for each sample.

$$PDF(D) = \frac{1}{\sigma\sqrt{2n}} e^{-\frac{-(D-D_m)^2}{2\sigma^2}} \quad (1)$$

TG analysis was carried out with the aid of a NETZSCH STA 409 PC/PG thermal analyzer. Samples were heated from 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 $\pm 1 \mu\text{g}$. A solid sample of about 15 mg was used in each test.

RESULTS AND DISCUSSION

Fig. 2 shows the X-ray diffraction pattern of RHA. The conditions employed for rice husk calcination produces amorphous silica, as is evident from a broad hump at the 2θ between $15\text{-}30^\circ$ in the diffraction pattern. This result is suitable for the synthesis because the silica is rendered active in its amorphous form to produce zeolites. It has been reported that calcination at higher temperatures or larger times produce crystalline phases of SiO₂ such as cristobalite, tridymite and α -quartz [14, 20, 26], which are difficult to dissolve.

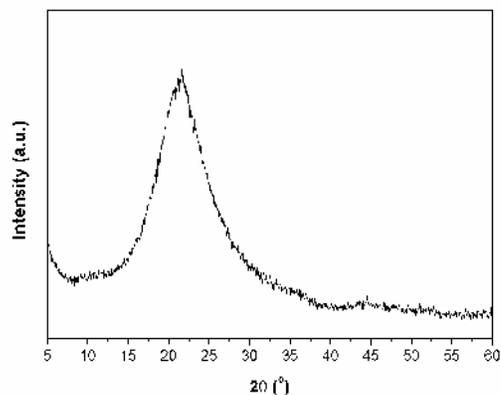


Fig. 2. X Ray Diffraction pattern of rice husk ash obtained at 700 °C for 2 hours.

The results of thermogravimetric analysis for serie I zeolites synthesized without and with surfactants as template are shown in Fig. 3. The DTG curve for the zeolite synthesized without template shows three

minimums at temperatures around 97, 170 and 407 °C. The first loss of mass corresponds to the removal of free and physically adsorbed water, while the two others are related with the loss of water molecules coordinated to the Na ions and inside the sodalite cage cavities, respectively [27, 28].

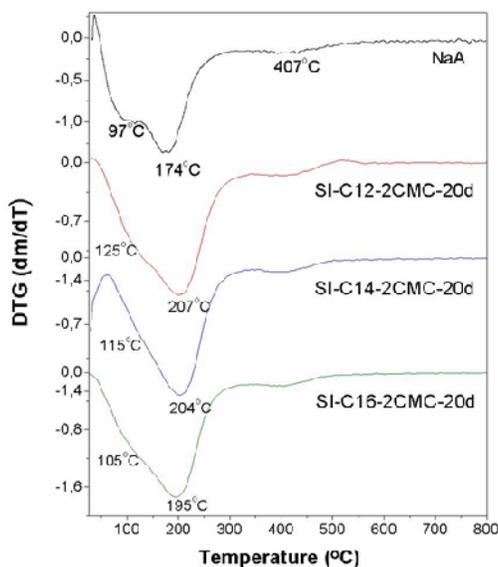


Fig. 3. DTG curves of serie I zeolites obtained without (NaA) and with templates at a concentration of two times their CMC value and aged for twenty days.

In samples synthesized using templates the first minimum appears as a shoulder and at higher temperature. The loss of water coordinated to the Na ions take place at higher temperature, together with the loss of surfactant decomposition products that occurs between 140-280 °C [29]. Meanwhile the loss of water inside the sodalite cage cavities take place at the same temperature. The absence of peaks related to the decomposition of the surfactant beyond 300 °C allowed us to select this temperature for the calcination of the samples, in order to eliminate the template used in the synthesis.

The X-ray diffraction patterns of selected samples of serie I and serie II zeolites are shown in Fig. 4 and Fig. 5, respectively. For serie I samples all the diffractograms match the reference pattern of NaA zeolite (PDF number: 01-089-8015) and no others zeolitic phases appear. There are not significant differences between the diffraction

patterns of these samples and those prepared at higher concentration of each template (4 CMC). In addition, no differences were observed in the diffraction patterns when increasing the length of the hydrocarbon chain of the surfactant, suggesting that the microporous structure of the zeolite is independent of the mesoporosity generated by the presence of the template.

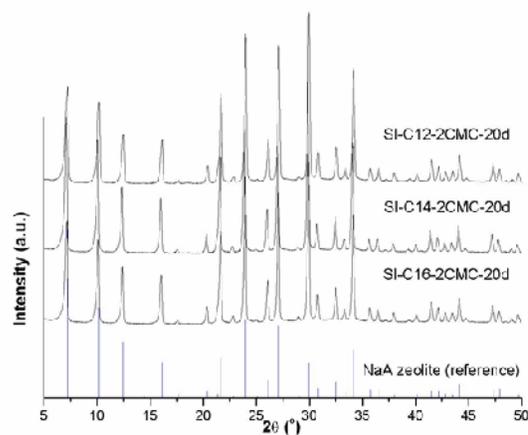


Fig. 4. X ray diffraction patterns of serie I zeolites synthesized with surfactants of different chain length as template.

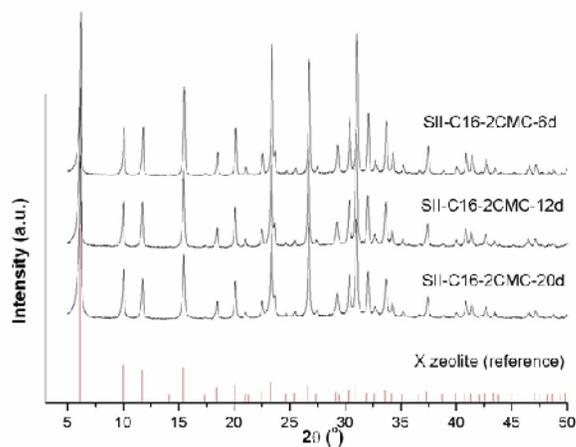


Fig. 5. X ray diffraction patterns of serie II zeolites synthesized with C16 surfactant as template for different aging time.

For serie II samples the diffractograms match the reference pattern of X zeolite (PDF number: 01-070-2168) and no others zeolitic phases were detected. There are not significant differences in the position of the diffraction peaks but a slight broadening of them is observed with the increase of the aging time. Similar

behavior is observed with the increase of the surfactant concentration. Such broadening of the diffraction peaks is probably due to the decrease in the particle size.

The SEM micrographs and particle size distribution histogram obtained by microscopy analysis for selected samples are presented in Fig. 6.

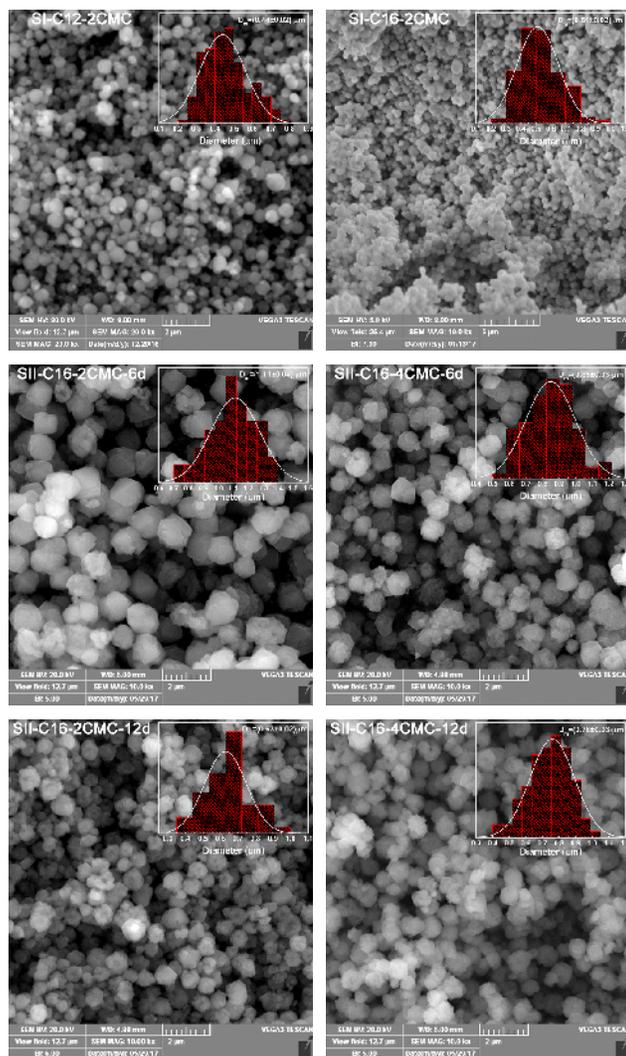


Fig. 6. SEM images, particle size distribution histograms and log normal fitting for selected samples.

For serie I samples the particle have a uniform morphology -cubic of smoothed edge- characteristics of zeolite A. The samples present a narrow particle size distribution with average size of particles around 0.5 μm (see Table 1). No significant changes are observed in the morphology and the size of the particles when increasing the concentration of surfactant or the hydrocarbon chain

length. Serie II samples have an octahedral morphology characteristic of the faujasite phase. The samples present a less narrow particle size distribution than serie I samples, with the most amount of particles in the range of 0.8 to 1.4 μm (see Table 1). It is important to note that the size of the particles decrease with the increase of the surfactant concentration and the aging time. These results corroborate the broadening of the peaks observed in the diffractions patterns of these samples.

Table 1. Mean particle size of selected samples

SAMPLE	Dm (μm)
SI-C12-2CMC-20d	0.44 ± 0.02
SI-C16-2CMC-20d	0.51 ± 0.02
SII-C16-2CMC-6d	1.11 ± 0.04
SII-C16-4CMC-6d	0.85 ± 0.03
SII-C16-2CMC-12d	0.63 ± 0.02
SII-C16-4CMC-12d	0.76 ± 0.03

The chemical composition of the samples, determined by EDS is presented in Table 2. As can be see serie I samples have a Si/Al ratio of about 1, as in the synthesis gel, while serie II samples present a Si/Al ratio of about 1.25, below the ratio formulated in the synthesis gel. Both Si/Al ratio are typical of A and X zeolite, respectively.

Table 2. Chemical composition of selected zeolites determined by EDS (w %).

SAMPLE	Si	Al	O	Na	Si/Al
SI-C12-2CMC-20d	14.9	14.6	58.4	12.1	1.02
SI-C12-4CMC-20d	13.2	13.3	62.3	11.4	0.99
SI-C14-2CMC-20d	14.8	14.5	58.4	12.5	1.02
SI-C14-4CMC-20d	14.9	14.4	58.8	12.0	1.03
SI-C16-2CMC-20d	16.6	16.1	54.2	13.2	1.03
SI-C16-4CMC-20d	14.6	14.4	58.7	12.2	1.02
SII-C16-2CMC-6d	11.3	9.13	71.5	8.1	1.24
SII-C16-4CMC-6d	14.0	11.4	64.4	10.2	1.23
SII-C16-2CMC-12d	11.9	9.8	68.2	10.1	1.22
SII-C16-4CMC-12d	14.3	10.8	65.0	10.0	1.32

CONCLUSIONS

The results demonstrated that it is possible to synthesize A and X zeolites at moderate temperatures, short crystallization times, without seeding, and with a good purity starting from rice husk ash as silicon source, instead of pure chemicals. In addition, in this work the synthesis procedure is performed at moderate temperatures, short crystallization times and without seeding. The use of this agricultural by-product and the employed synthesis procedure, reduces the economic cost of the synthesis of a product with high added value such as zeolites.

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