



SYNTHESIS OF GREEN ZEOLITE USING SOLID WASTES AS SILICON AND ALUMINUM SOURCE

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ABSTRACT: The X/A zeolite crystals mixtures were synthesized using sugar cane bagasse (SCBA) as silicon source and multilayer food packing (MFP) as aluminum source under hydrothermal condition at 80 °C for 79-296 h. The silicon was extracted by alkaline fusion for 40 min, at 550 °C with an alkali:SCBA ratio of 1:1. The aluminum solution was obtained from MFP using NaOH 1M (3:1 water/acetone) solution. The synthesized zeolites were analyzed by XRD, FTIR, SEM and BET. In XRD results, all signals were indexed to zeolite X and some signal zeolite A. The vibration bands at region 1200-400cm⁻¹ suggested the presence of double-six-ring (D6R) zeolite X structure. The crystal morphology is characteristic of the zeolite X and the specific area found by BET method was 600.34 m²/g. Therefore, the synthesized material has potential applications as a catalyst, as adsorbent, and as an ion exchanger.

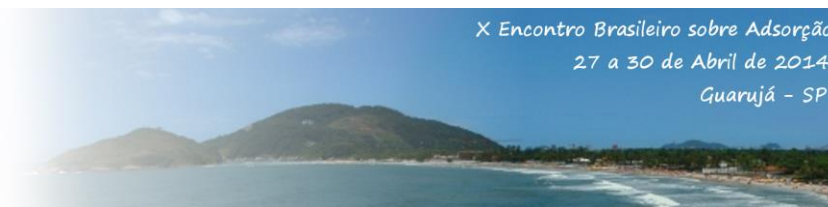
KEYWORDS: microporous materials, solid waste, environmental science, recycling, crystal growth.

1. INTRODUCTION

Zeolites are aluminosilicates of the alkaline and alkaline-earth metals with porous framework structures of corner-sharing SiO₄ and AlO₄ tetrahedral. Many industries use these materials and decreasing production cost is relevant. One of the promising strategies to prepare zeolites at low cost is to replace commercial chemicals with waste products as the starting precursor (Witton and Chareonpanich, 2012). The disposal of large amounts of sugarcane bagasse ash and multilayer food packing has become a serious environmental problem. However, these solid wastes can be used in zeolite synthesis process.

Sugar cane bagasse is a hazardous solid waste generated in large amounts in sugar mills. Combustion of sugar cane bagasse in boilers, used for steam and electricity generation, produces a great amount of another solid waste, denominated sugar cane bagasse ash (SCBA) (Balakrishnan and Batra, 2011). Employing this quartz-abundant waste as a silicon source can avoid its accumulation (Moises *et al.*, 2013).

The food packaging industry needs to develop multilayer films, containing different polymers. Multilayer films may be films gathered in the factory or turned into waste. Thus, the future of multilayer packages has become a great environmental concern.



Most researchers have used wastes as a low-cost silicon and aluminum source to produce zeolites. Different types of zeolites such as X (Tanaka and Fujii, 2009) (Jha *et al.*, 2009), ZSM-5 (Chareopanich *et al.*, 2004), hydroxysodalite (Tanaka and Fujii, 2009) (Shigemoto *et al.*, 1993), Na-P1 (Inada *et al.*, 2005) (Hollman *et al.*, 1999) and zeolite A (Moises *et al.* 2013) (Querol *et al.*, 2001) were synthesized through many methods. Considering this, zeolite synthesis is a promising technique to recycle these wastes and has received extensive attention over the last decade.

The purpose of this study was to synthesize zeolite using SCBA as silicon source and MFP as aluminum source. This research demonstrates the potential of SCBA and MFP extract to be used as a reliable silica and aluminum source for preparing zeolites.

2. EXPERIMENT

The sugar cane bagasse ash (SCBA) was collected from sugar cane industry located in the region of Maringá City, Paraná, Brazil. The quartz material was placed in a horizontal furnace and heated it in air at 20°C/min from room temperature to 600 °C and kept it for 4h (SCBA600). Our prior work has characterized these materials (Moises *et al.*, 2013). Inovaflex Rótulos e Etiquetas (Maringá, PR – Brazil) supplied the parings of multilayer film containing 19.0±1.0 wt% of PET, 47.0 ± 1.0 wt% of PE and 34.0 ± 1.0 wt% of Al. The films were cut to 200×300 mm. Treating MFP with NaOH yielded the aluminum solution 1 mol/L (3:1 water/acetone) after 24 hours. After silicon and aluminum extraction, both solutions were mixed as 1SiO₂:0.4Al₂O₃:3.3Na₂O:173.8H₂O. The mixture (2.0 L) was transferred to 10 polypropylene reactors (0.2 L each) and kept it 80°C for different crystallization periods (79, 121, 149, 163, 212, 235, 247, 272, 284, and 296 h). Then, the solid was separated by filtration, washed it with distilled water and dried it overnight at 100°C.

Characterization: The zeolites were characterized by Fourier transform infrared spectrometry (Bomem-Michelson MB-100 with a resolution of 4 cm⁻¹ using a KBr) and XRD analysis (Shimadzu, model XRD-6000 X-ray operated at 40 kV and 40 mA, with Cu Kα (1.54Å) as the radiation source, diffraction angle - 2θ - in the range 4° - 60°). The relative crystallinity was determined using a diffraction signal localized in

2θ = 6.11 and sample 79 h as standard. Scanning electron microscopy (SEM) (Shimadzu SSX-550 Superscan) characterized the morphology and the N₂ adsorption/desorption isotherm applying BET method (ASAP 2020 – Micromeritics) revealed the surface area.

3. RESULTS

Figure 1 displays the X-ray diffraction patterns of zeolite synthesis for each period of time. The diffraction peaks to zeolite type X and A were indexed as indicated inset the figure. These zeolites exhibit Pm-3m and Fd-3 space groups respectively (standard pattern number 71-0784 and 85-2064 - ICDD database and standard pattern of International Zeolite Association - IZA). After 79 h, X/A zeolite crystals mixtures were detected. Following the crystallization time, zeolitization increases until 149 h. After 149 h, crystallinity decreases, indicating an alkaline attack due to high crystallization time. This can be observed in the signal to zeolite X (crystallographic plane [111] localized in 6.11 (2 theta degree). The materials with higher relative crystallinity were 149, 163 and 212 h. Available times verify Ostwald's rule (Anseau, 1973): the crystalline phase did not change successively, indicating that increasing time will not obtain pure phase zeolite X.

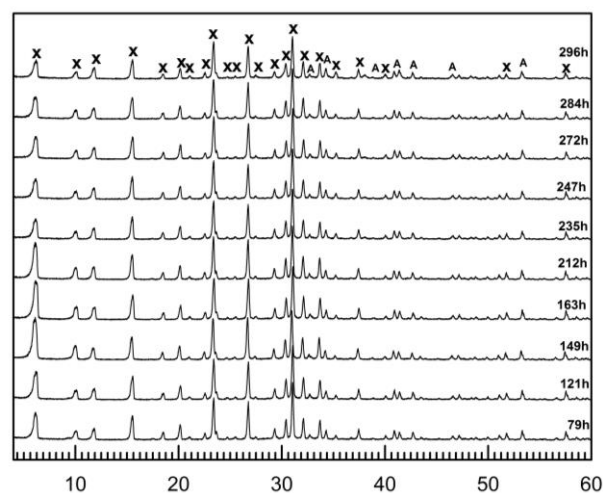
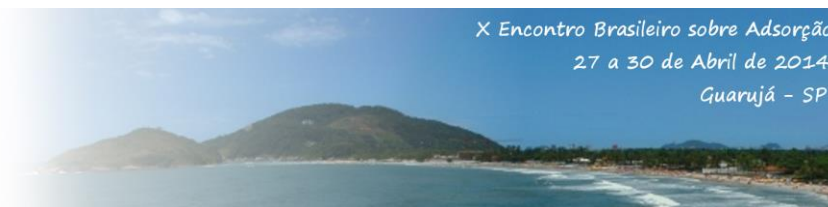


Figure 1. XRD results of zeolite synthesis as a function of time in hydrothermal process.

Figure 2 presents the FTIR spectra of the zeolites as a function of hydrothermal process period. The existence of zeolite X is suggested by peaks in the lattice region of 1200–400 cm⁻¹. The spectrum of X zeolite illustrates the presence of



absorptions at 458, 559, 666, 746 and 974. The 974 cm^{-1} band is due to the Si–O–Al asymmetric stretching vibration mode of T–O bonds, (where T = Si or Al). The band at 746 cm^{-1} is due to the S4R T–O–T symmetric stretching, while the absorption at 559 cm^{-1} is attributed to D6R T–O–T symmetric stretching and is very close to external vibration of double four-rings (D4R) in for zeolite A framework localized in 557 cm^{-1} . The two bands at 666 and 458 cm^{-1} are assigned to the Si–O–Al symmetric stretching and S4R symmetric bending modes, respectively. This band is slightly shifted and sharpens as the amorphous material transforms to crystalline zeolite. These results agree well with XRD and microscopy results. The OH band, related to deformational vibrations of adsorbed water molecules in zeolite channels, also appeared at about 1655 cm^{-1} (Yao *et al.*, 2009).

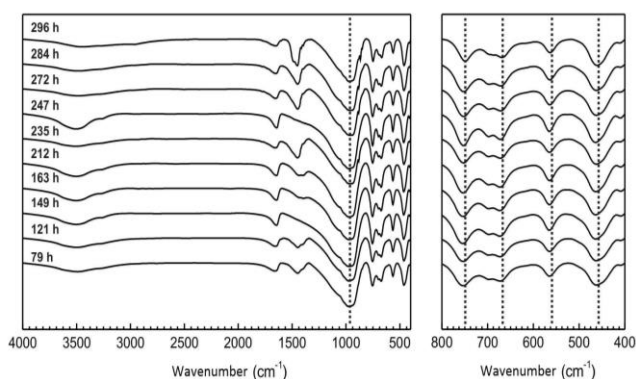


Figure 2. FTIR results of e evolution zeolite synthesis as a function of time in thermal process.

The SEM observations in Figure 3 surveyed the external morphology of synthesized zeolites in different periods. A well-defined octahedral morphology is typical of zeolite X (Tanaka and Fujii, 2009) (Jha *et al.*, 2009) and appeared in hydrothermal synthesis of 79 hours. After 212 h, corrosion surface set in, indicating alkaline attack on the surface due to high crystallization time. This evidence corroborates XRD and FTIR results.

The specific surface area of materials with higher crystallinity synthesized by 149, 163 and 212 h was measured by nitrogen adsorption–desorption isotherms at 77 K. The BET method obtained the total specific surface area (we chose the linear region in the range 0.05 <P/P0< 0.3) were 600.34 m^2/g , 582.12 m^2/g and 527.21 m^2/g to materials 149 h, 163 h and 212 h respectively. This area is large and close to that found by other researchers. The zeolite at 149 h exhibits a higher

specific area surface, corroborating with XRD results that indicate 149 h material presented higher relative crystallinity. This fact points to a potential application of this green material, because zeolite X has a large pore size (7.3 Å) and a high CEC (5 meqg^{-1}), which make this zeolite an interesting molecular sieve and a high-cation exchange material (Querol *et al.*, 2002).

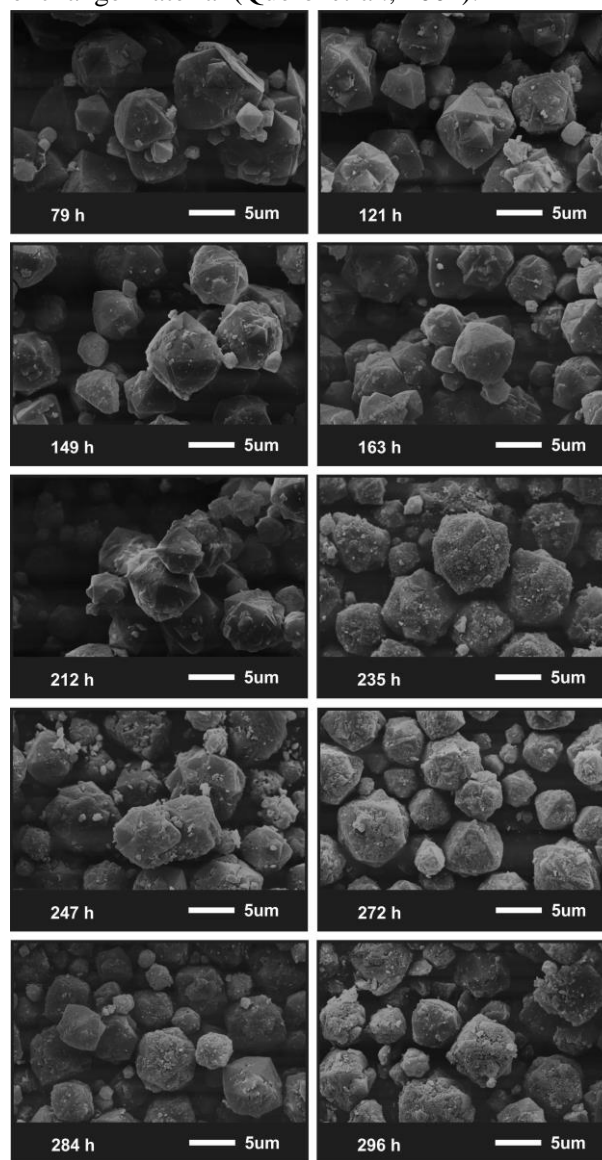
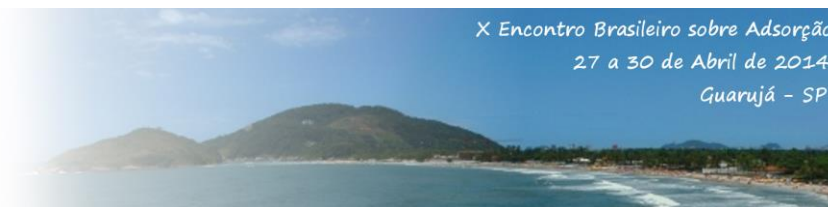


Figure 3. SEM Micrographs of zeolite crystallization process.

4. CONCLUSIONS

This work showed that sugar cane bagasse ash and multilayer food packing can be successfully used as raw material for the hydrothermal synthesis of green and low-cost



zeolites, which have potential applications in adsorption, catalysis, and ion exchangers. This research contributes to materials and environmental science, suggesting the recycling of a contaminant solid waste generated in large amounts around the world.

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6. ACKNOWLEDGMENTS

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