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# A Low Cost ZSM-5 Zeolite Obtained from Rice Hull Ash

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**Abstract** The high pure synthetic zeolite have a large application in industry and agriculture, being nowadays in majority imported in Brazil. The biomass like rice hull ash (RHA), a rice industry waste, can be real advantageous in manufacture of different materials, since that is produced in large scale in the country. The silica extraction from RHA by alkaline leaching is a low energetic cost process and high efficiency, obtaining high pure silica with high reactive amorphous structure, very interesting for zeolite production. In this work was developed a economically feasible route for the production of high purity and crystallinity ZSM-5 zeolite, free of expensive template, starting from a low value intake, a industrial waste, producing a high value materials. The extracted silica from RHA in sodium silicate form is precipitated in the proper zeolite formation reactional mixture. The ZSM-5 have a lot of industrial applications due your high selectivity in catalytic reactions and high thermal and acid stability.

## Introduction

Zeolites are crystalline microporous aluminosilicates consisting of tetrahedral units of  $[\text{SiO}_4]^{4-}$  and  $[\text{AlO}_4]^{5-}$ , linked by all their corners, that create a *sui generis* system of channels with molecular dimensions. In this structure of many cavities and pores are located water molecules and cations that are determined by the numbers of  $[\text{AlO}_4]^{5-}$  tetrahedra in the framework[1]. Zeolites are very efficient ion exchangers, molecular sieves, drying agents and shape-selective catalysts that are consequence of well-defined crystalline structure, high internal surface area, uniform pores, good thermal stability and cation mobility[2]. The medium pore size ZSM-5 zeolite, with MFI structure and high Si/Al relation, represents a continuing area of interest for process involving petrochemicals and fluid catalytic cracking like cracking, hydrocracking, isomerization, alkylation and reforming reactions. ZSM-5, for instance, has a three-dimensional system linked via intersections rather than cavities and mordenite (other zeolite structure with 5-1 secondary building unit) catalysis seems to take place only in the largest channels. In general, ZSM-5 synthesis use a organic template in the mixture that direct the porous structure grow. There are many disadvantage in organic template use. Since the synthesis of ZSM-5 must be carried out under pressure while heating,

these organic templating agents are environmental hazard once released into the atmosphere or water system. Further, these compounds add to the cost of producing, for instance, TPA alone often makes up as much as 50% of the production costs of ZSM-5 in prior art processes. Removing the templating agent, which is accomplished by combustion can result in the cracking and degradation of the lattice structure of ZSM-5[6].

Different methods to obtain silica affect your structure and morphology that influence the reactivity. The amorphous silica is very active and important to zeolite synthesis. There are two methods to obtain silica from RHA, calcination with controlled atmosphere (between 500-700°C) and alkali leaching. The first consume too much energy and produce a crystalline silica with low reactivity. In the second amorphous silica from RHA can be extracted using low temperature. The solubility of amorphous silica is very low at  $\text{pH} < 10$  and increases sharply at  $\text{pH} > 10$ . This unique solubility behavior enables silica to be extracted in pure form from RHA by leaching under alkaline conditions[3].

## Experimental Procedure

A RHA from São Gabriel-RS, Brazil, burned at 1100 °C to produce energy was used. This high temperature guarantee a very low organic compounds impurities, a chemical and crystallographic analysis was made. The leaching was carried out at 90°C in 1N NaOH solution and different RHA mass, in the 1:1; 1:2; 1:2,5; 1:3; 1:3,5 and 1:4 relations. From the better  $\text{SiO}_2/\text{Na}_2\text{O}$  molar relation, close to 3,50, in the sodium silicate solution was made the reactional mixture. At vigorous stirring was added sodium hydroxide to a molar ratio  $\text{OH}^-/\text{SiO}_2 = 0,60$ ; aluminum sulphate to  $\text{Si}/\text{Al} = 33,0$  ratio; sodium sulphate to  $\text{SO}_4^{2-}/\text{SiO}_2 = 0,5$  ratio; ethanol/ $\text{SiO}_2 = 0,35$ ; and ZSM-5 seeds at 0,1% of total mass. The sulphate ion has in basic medium influence in crystal size, increasing with sulphate concentrate and decreasing the ratio length/width of crystal[4]. The mixture was aged for 40 hours at 40°C in thermostatic bath. Then the gel was charged into teflon-lined stainless-steel autoclaves and crystallized by thermal treatment under autogenous pressure and static conditions at 200°C and 50 hours. There was studies of ZSM-5 at 90°C and atmospheric pressure, however it has been pointed out as a disadvantage that a prolonged not competitive crystallization time of 8 to 11 days is required to reach 100% crystallization[9]. After crystallization, the solid was filtered, washed several times with distilled water and dried at 120°C for 24 hours.

Chemical analyses were performed by X-ray fluorescence (XRF) with a PHILIPS PW 1480 spectrometer. The X-ray diffraction (XRD) patterns was obtained with a SIEMENS diffractometer with  $\text{CuK}\alpha$  radiation. The specific surface area and microporous volume was measured with  $\text{N}_2$  at 77 K using the GEMINI 2370 from Micrometrics. The total microporous volume was obtained from nitrogen adsorption isotherms at  $P/P_0 = 1$  and specific surface area (BET) at  $P/P_0 = 0,3$ .

## Results and Discussion

On a commercial burning of RHA as an energy source, the resultant ash had the following chemicals analysis (by weight):  $\text{SiO}_2 = 87-92\%$  and carbon = 8-12%. The remaining impurities consists of minor amounts of magnesium, potassium, iron, aluminum, calcium and sodium. Apparently, it is these metal salts, as well as organic material, which impart the amber color to the silicates an which are very difficult to remove once the soluble silicate is formed. The carbon content was in a dispersed state throughout the material.

Depending upon the time and temperature of burning of biogenetic source silica, and the particular furnace used, the carbon can vary considerably, for example, up to and above 12%. The XRD pattern from RHA showed two phases, one amorphous (silica) and cristobalite and was not quantified each one. Table 1 has the results of leaching with different RHA/NaOH relations. The best relation is 3:1 that has good SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio and total solids is slight less than ideal, a small water removing by evaporating was necessary.

Table 1 Sodium silicate solution analysis.

RHA/NaOH	1 : 1	2 : 1	4 : 1	2,5 : 1	3,5 : 1	3 : 1
Na <sub>2</sub> O (%)	3,146	2,883	3,110	2,475	2,605	1,732
SiO <sub>2</sub> (%)	3,978	5,546	9,756	6,082	7,775	6,035
H <sub>2</sub> O (%)	92,876	91,572	87,134	91,443	89,620	92,233
Total Solids (%)	7,124	8,429	12,866	8,557	10,380	7,767
SiO <sub>2</sub> / Na <sub>2</sub> O	1,26	1,92	3,14	2,46	2,98	3,48
Density at 25°C (g/l)	1.068	1.074	1.108	1.070	1.084	1.068

The figure 1 shows the X-ray diffraction pattern of zeolite resulted, the crystallographic phase formed is ZSM-5. A narrow and high peaks denoted a very good crystallinity. The gel chemistry control avoided undesirable mordenite phase. Even though ethanol by itself was not effective as a template, it has a co-template function attributed to its ability to modify the gel chemistry[5]. With ZSM-5 seeds the high crystallinity of desired phase was succeed.

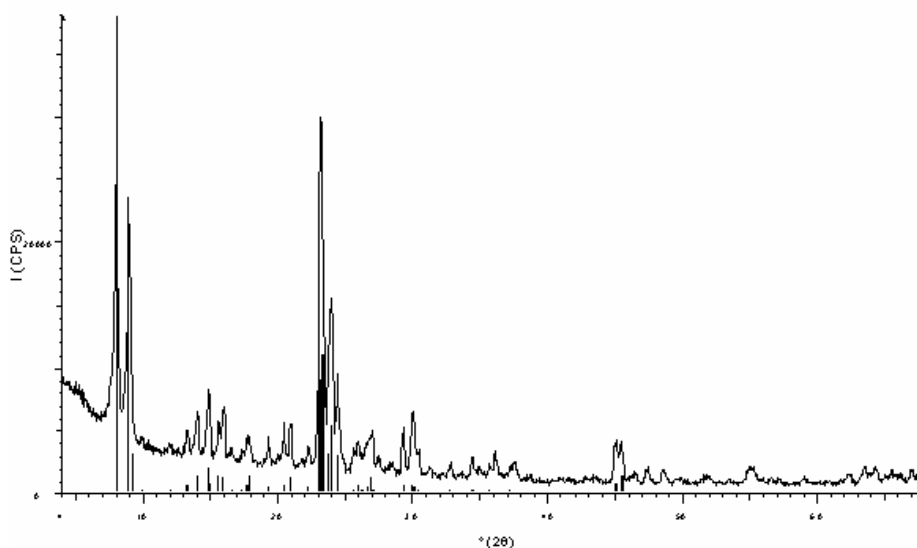


Fig.1 X-Ray diffraction pattern of ZSM-5 obtained.

The chemical analysis by X-Ray fluorescence was LOI = 5,1%, SiO<sub>2</sub> = 91,1%, Al<sub>2</sub>O<sub>3</sub> = 2,4%, Na<sub>2</sub>O = 1,1%, Fe<sub>2</sub>O<sub>3</sub> = 0,08%, TiO<sub>2</sub> = 0,06% and CaO = 0,05%, how expected a high silica zeolite with Si/Al ratio = 33,5. As a general experience, the Si/Al ratios of the crystallized zeolites increase with decreasing excess alkalinity and increasing Si/Al ratio in the batch[8]. Some related zeolites crystallizing from batches can be described by Eq. 1.

$$(\text{Si}/\text{Al})_{\text{zeolite}} = 1 + b([\text{SiO}_2]/[\text{OH}^-])_{\text{solution}} \quad (1)$$

For zeolites with five-membered ring structures values of  $b = 7-10$  proved to be suitable. It could be shown that this equation would be a good help for planning synthesis of mordenite, template-free ZSM-5 and BETA[8]. It is difficult to crystallize ZSM-5 with Si/Al ratios above 35 without using a template. The lower limit is at about Si/Al = 10. For batches giving lower Si/Al ratios, mordenite is obtained.

The RHA burned at high temperature was fundamental to avoid undesirable organics phases in sodium silicate, and with the efficiency of leaching process in separate impurities, resulted in high purity zeolite.

The specific surface area was 320,7 m<sup>2</sup>/g and micropore volume was 0,106 cm<sup>3</sup>/g. This high values demonstrated a good crystallinity, small particle size and no crystalline degradation in ethanol and moisture removing at 120°C. Among the various functional groups, alcoholic and amino group containing molecules have enjoyed wide success as templates. The frontier molecular orbitals of amines have larger energy than the alcohols but they are invariant to the position of the functional group, thus the alcohols may be better electron withdrawing compounds than the amine[10].

## Summary

A very low cost and environmental advantageous ZSM-5 zeolite synthesis was achieved. A low energy chemical method with worthless residue raw material was successful to obtain high active pure sodium silicate. The cheaper and less hazardous organic template-free process synthesis, without high temperature treatment after crystallization propitiated a high crystalline and well-defined phase ZSM-5 zeolite. Nearly 18 years passed between the initial discovery of ZSM-5, at MOBIL labs, in 1965 and its first scale commercial trial in a cracking unit in 1983. Prior to the commercialization of ZSM-5, all zeolites were manufacture by low-temperature, template free and atmospheric pressure synthesis[7]. ZSM-5 large production still a continuous development aimed economical benefits.

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