RICE HUSK BASED ZEOLITE AS METHANE ADSORBENT¤

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ABSTRACT

Rice husk ash (RHA) is a good alternative source for the production of zeolite since it contains more than 95% silica. The content of silica and carbon in rice husk were varied depending on combustion temperature, thus varies the properties of zeolite produced. Unlike typical post synthesis modification where non-polar materials are introduced into zeolite structures, carbon is included into zeolite during the hydrogel formation as it is present in RHA. To study the potential use of RHA based zeolite on gas adsorption, RHAs obtained from different combustion temperatures (450 – 800°C) will be used to synthesize zeolite under hydrothermal condition. The differences in structural properties and gas adsorption characteristics from different RHAs were analysed. It was found that RHA properties affect structural formation of zeolite, physicochemical properties as well as methane adsorption behavior.

Keywords: Rice husk, carbon, zeolite, gas adsorbent.

1 INTRODUCTION

Synthetic zeolites are produced in large quantities from various kinds of silica sources such as volcanic ash, fly ash and metakaolinite. But the presence of impurities limits the use of these resources. Several studies show that rice RHA has been used as a source of silica for the production of zeolites (Hamdan et al., 1997, Wang et al., 1998, Ramli et al., 2000, Yalcin and Sevinc, 2001). As reported by Hamdan (2002), there are about 100,000 million tons of rice husk produced annually in Malaysia that can create environmental problems. Since landfilling is expensive, incineration under controlled condition is adopted as a method of reducing the waste. But with high silica content in the ash, it can be utilized as silica source for production of silicon carbide, cement, concrete or zeolites. Other components in RHA are carbon, water vapor and trace metals such as calcium, potassium and magnesium (Zainab et al., 1996). Different combustion conditions will subsequently yield different amount of carbon left in the RHA.

The presence of carbon in rice husk ash during zeolite synthesis could increase surface hydrophobicity and decrease zeolite polarity, as carbon is a non-polar element. This could be an alternative method to increase hydrophobicity of zeolites and increase adsorptive affinity of several types of hydrocarbon. Studies by Ramli et al. (2000) and Hamdan et al. (1997) showed that amorphous silica from rice husk was highly active for zeolite synthesis but the presence of crystabolite and tridynamite caused inactiveness

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towards zeolite synthesis. The formation of crystabolite, tridynamite or other crystalline structures depends on operating conditions, combustion temperature and heating rate. Rice husk based zeolite can be prepared from a mixture of sodium silicate containing silica from RHA and sodium aluminate. The presence of carbon, metal and other impurities may also affect zeolite properties and hence, adsorption characteristics.

Zeolite has been recognized as a good gas adsorbent in many industrial processes due to the unusual crystalline structures and unique physicochemical properties. The adsorption characteristic of any adsorbent depends on adsorbent physicochemical properties, structure, and adsorbate physical properties. This adsorption process involve three consecutive steps namely mass transfer of the adsorbates by diffusion, from bulk fluid to the external surface of adsorbent, diffusion through the pore window to the surface of adsorbent, and adsorption on the surface. Normally, the adsorbates are physically adsorbed on the surface by van der Waal forces and electrostatic interaction that existed between gas molecules (adsorbates) and atoms that compose the adsorbent surface. This mean that gas adsorption rate and capacity is mainly controlled by physicochemical properties of adsorbent which in turn is determined by reactants and experimental conditions used in the synthesis. Thus, this paper will discuss the effect of combustion temperature on RHA and zeolite structural formation and methane adsorption characteristics.

2 EXPERIMENTAL

2.1 MATERIAL

The rice husk used was obtained from the local rice mill. All chemicals used in this research are of analytical grade. Sodium hydroxide pellets (MERCK, 99%) and sodium aluminate anhydrous (Riedel-de Haën, 99.95%) were directly used without purification. Distilled water was used in the synthesis, preparation of solution and washing to minimize the presence of impurities. Methane (99.99%) obtained from SIG Sdn. Bhd. was used for adsorption study.

2.2 ZEOLITE SYNTHESIS

The rice husk was directly combusted without any pre-treatment in the furnace (Carbolite, Eurotherm 2480 CP). Combustion was carried out at three different temperatures (450°C, 600°C and 800°C) with heating rate of 5°C / min. The samples were then held at the selected temperature for 2 hours. Three samples of rice husk based zeolite were prepared from reaction mixture ratio of 6.8 Na_2O: 12 SiO_2: Al_2O_3: 240 H_2O where silica source was obtained from RHA combusted at different combustion temperatures (450ºC, 600ºC and 800ºC). In preparing gel composition, sodium aluminate (Riedel-de Haën) was dissolved into sodium hydroxide (MERCK) solution followed by heating under rigorous stirring. The silica from RHA was extracted by digestion of RHA with NaOH at 80 ºC for at least two hours. Both solutions were mixed and stirred for 2 hours to obtain a homogeneous mixture which was then transferred into a polyethylene bottle and heated in the oven at 100ºC for 14 hours. The solid formed were recovered by filtration, washed with distilled water until pH <10 followed by drying overnight in the oven at 100^oC.

Zeolites obtained from the synthesis were characterized by X-ray diffraction (XRD) in order to investigate the structural formation. This measurement was conducted in the range of $5° \leq 2\theta \leq 50°$ at room temperature. Nitrogen adsorption analysis (Quantrachrome 1000) was carried out at 77K to determine specific surface area, pore volume and average pore diameter of the sample.

2.3 METHANE ADSORPTION MEASUREMENT

Methane adsorption measurement was carried out using Thermal Gravimetric Analyzer (Perkin Elmer, TGA 7) carried at 1.3 bar and 50°C. Zeolite samples were loaded on the sample pan and outgassed at 400°C for at least 1 hour. The samples were then cooled and held at 50°C for adsorption to occur until it reached equilibrium.

3 RESULT AND DISCUSSIONS

3.1 STRUCTURAL PROPERTIES

As reported in literature, amorphous silica is highly reactive and can be used in the synthesis of zeolite. RHA samples (RHA-450, RHA-600 and RHA-800) combusted at three different temperatures are amorphous as indicated by the featureless diffractograms (Figure 1). Nevertheless, a small peak is observed at $2\theta = 22°$ in the diffractogram for RHA-800, which corresponds to crystalline phases. The intensity of this peak is relatively low, hence the crystalline phase is not pronounced in RHA-800. RHA-800 is still in the amorphous form although previous study done by Halimaton Hamdan et al. (1997) has shown that crystalline silica will be formed at combustion temperature above 700°C. However, all the three RHA samples produced in this study show diffused peaks with relatively high intensity at $2\theta = 13.4°$ instead at $2\theta = 22°$.

Zeolites in the form of fine white-brown solids were obtained from the hydrothermal synthesis of zeolites using the RHA samples combusted at different temperatures. Figure 2 represents the XRD patterns of the zeolite samples in comparison with the commercial NaY zeolite. The positions of the peaks (2θ = 15.45°, 18.48°, 20.10°, 23.37°, 26.74° and 31.02°) in the XRD pattern of RHA-450 are in good agreement with the NaY although the intensity of these peaks are relatively much lower than NaY. The XRD pattern of ZEO-600 is almost featureless except for a few not-well-resolved peaks at 2θ =23.39° and 26.80°. Therefore, ZEO-600 is primarily amorphous phase. The XRD pattern in Figure 2(c) shows that zeolite phase other than the faujasite-typed is present in RHA-800. The existence of peaks at 2θ = 21.64°, 24.30° and 28.08° which correspond to the zeolite P, indicates the presence of zeolite P instead of zeolite Y in ZEO-800. The formation of zeolite P might be due to the silica source from RHA-800 which is not reactive towards the formation of zeolite Y. Studies by Ramli et al. (1996) have shown that zeolites synthesized from less reactive RHA silica consist of a mixture of zeolite Y and P.

As discussed earlier, RHA affect the structural properties of rice husk based zeolites produced. Nitrogen analysis reveals that the porosity of rice husk based zeolites is relatively lower than commercial zeolite (NaY). However, ZEO-450 has better porosity than ZEO-600 and ZEO-800 (Table 1). Crystalline phase indicates the porosity of the samples as shown by XRD pattern of NaY sample where high crystallinity leads to high porosity. Therefore physicochemical properties of rice husk based zeolites can be further improved by using active silica from amorphous RHA in synthesizing rice husk based zeolite.

Table 1: Properties of rice husk based zeolite obtained from nitrogen adsorption analysis.

Sample	Micropore surface area (m^2/g)	Micropore volume(cm^3/g)	Average pore diameter (nm)	Adsorption energy (kJ/mol)
ZEO-450	211	0.075	2.95	8.80
ZEO-600	90	0.032	5.40	4.81
ZEO-800	39	0.014	6.00	4.33

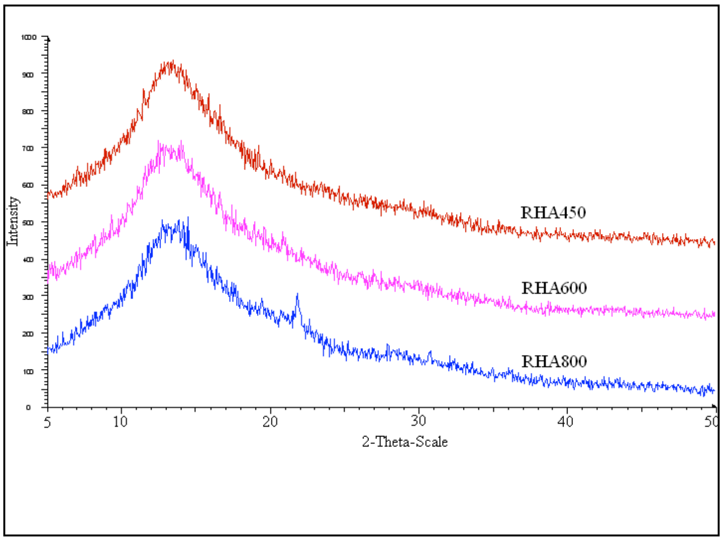

FIGURE 1: XRD patterns of RHA samples (RHA-450, RHA-600 and RHA-800).

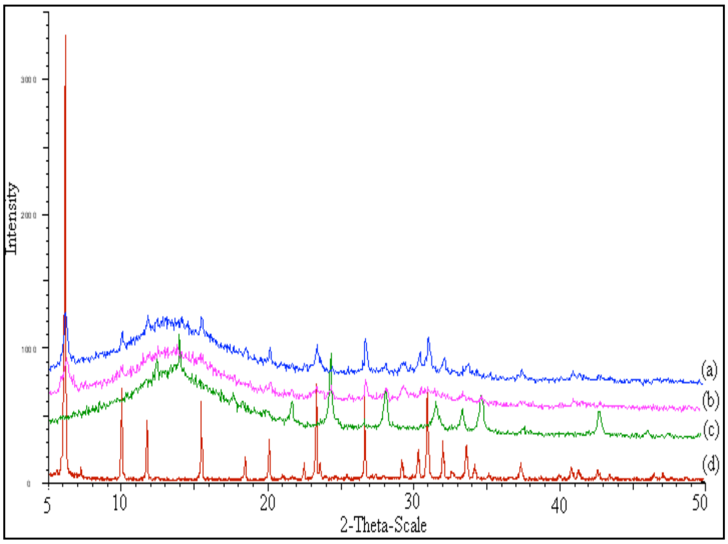

FIGURE 2: XRD patterns of zeolite samples: (a) ZEO-450; (b) ZEO-600; (c) ZEO-800; and (d) NaY.

3.2 METHANE ADSORPTION CHARACTERISTICS

Figure 3 shows the percentage weight of methane adsorbed on rice husk based zeolite (ZEO-450, ZEO-600 and ZEO-800). ZEO-450 shows high methane adsorption followed by ZEO-600, and ZEO-800. For comparison, methane adsorptions on other zeolite samples (NaX, NaY and Na-18) are also presented (Figure 4). Even though structural properties such as relative crystallinity, surface area and pore volume play a vital role in gas adsorption, rice husk based zeolite shows a promising performance as methane adsorbent. It is expected that at lower combustion temperature (450°C), more carbon still remains in RHA. Therefore, zeolite that was synthesized from RHA450 able to adsorb more methane than NaY and about the same amount as NaX (Table 2) even though the peaks intensities is relatively lower than NaY. This could be due to the presence of carbon in rice husk based zeolite that improves the adsorption even though structural formation is relatively poor. The results also show that with least carbon content (ZEO-800), the sample adsorbs less methane, lower adsorption rate and longer equilibrium time. The structural properties of rice husk based zeolite could be improved if highly active silica can be produced. The surface area, pore volume and average pore diameter of rice husk based zeolite is significantly lower than NaY (Table 1).

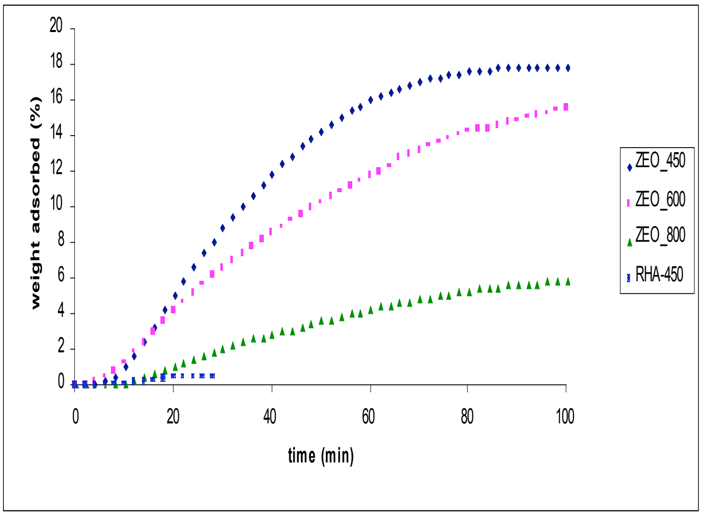

FIGURE 3: Methane adsorption on rice husk-based zeolite.

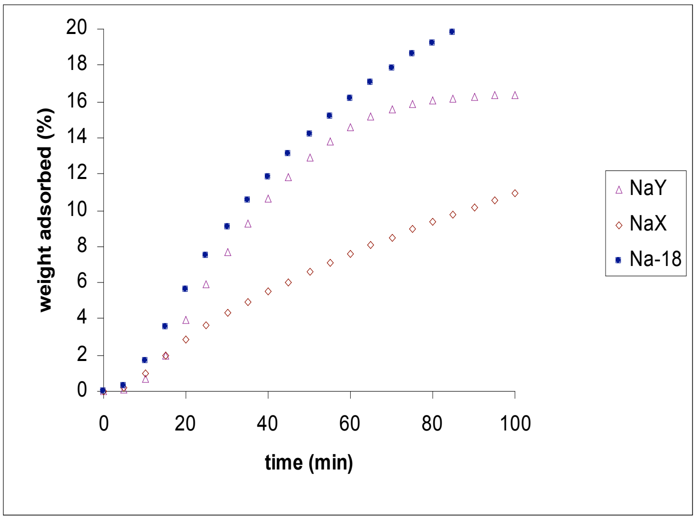

FIGURE 4: Methane adsorption on commercial zeolite (NaX and NaY) and synthesized zeolite from commercial silica.

TABLE 2: Adsorption of methane on rice husk based zeolites and commercial zeolites .

Sample	Adsorption capacity (mmol/g adsorbent)	Initial adsorption rate (mmol/sec) x 10^6	Equilibrium time (min)
ZEO-450	11.3	1.62	89
ZEO-600	10.3	1.51	123
ZEO-800	4.2	0.80	159
NaY	10.3	3.43	84
NaX	11.6	1.64	262
Na-18	13.8	3.56	125

4 CONCLUSIONS

Rice husk based zeolite has a great potential as methane adsorbent. By improving the combustion procedure, amorphous active silica can be obtained. Hence, zeolite structural formation and porosity can be improved, and with the presence of carbon in the RHA, the methane adsorption characteristics can be further improved.

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