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Contributed Paper

## SUZ-4 Zeolite Synthesis Derived from Rice Husk Ash

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### ABSTRACT

Rice husk ash (RHA) as a raw material was used to synthesize SUZ-4 zeolite via a hydrothermal process in the presence of tetraethyl ammonium hydroxide as the template. The molar ratios of silica from RHA:silica sol were varied as the following: 0:100, 50:50, 70:30, 90:10 and 100:0. The synthesized zeolite was characterized using various techniques including X-ray powder diffraction, scanning electron microscopy and BET-N<sub>2</sub> adsorption method. The results show that the obtained SUZ-4 zeolite using pure silica sol has a needle-shape crystal having diameter in a range of  $0.07 \pm 0.02 \mu\text{m}$  and length in a range of  $1.7 \pm 0.2 \mu\text{m}$ , while the SUZ-4 crystal from using 50% RHA has a larger needle-shape than that of pure silica sol, having diameter of  $0.2 \pm 0.01 \mu\text{m}$  and length of  $5.0 \pm 1.5 \mu\text{m}$ . The crystallite size was shrunk to  $0.13 \pm 0.01 \times 2.8 \pm 0.2 \mu\text{m}$  when 90% and 100% RHA were used. With 50 % RHA, high purity of SUZ-4 was obtained having the same surface area as that of 100 % silica sol. The increase in RHA content did change the pore size distribution due to the competitive formation of Merlinoite zeolite (MER) during the crystallization process.

**Keywords:** SUZ-4 zeolite, merlinoite (MER), rice husk ash (RHA), silica sol

### 1. INTRODUCTION

Biomass is a renewable resource with great utilization due to environmental considerations and the increasing demands of energy worldwide. Rice husk ash (RHA), a by-product of rice mill industry, is one of the alternative sources with high silica content and can be used for production of valuable materials and chemicals. The silica in RHA is amorphous and transforms to

crystalline silica when it is heated at high temperatures. Crystalline silica is recognized as a material that can cause damages to respiratory track and other tissues, and cancer according to the International Agency for Research on Cancer (IARC) announced in 1997. Finding an appropriate utilization of the ash is necessary to protect the environment and to decrease the

amount of RHA waste requiring storage area. There have been many researches encouraging the utilization of  $\text{SiO}_2$  from RHA for the synthesis of various types of zeolites and nanomaterials [1-8], the experimental results so far show its high potential for utilization, due to the differences in the nature of the RHA prepared and in the composition of the precursor gel.

There are approximately 175 unique zeolite frameworks identified by the International Zeolites Association (IZA) [9] and over 40 naturally occurring zeolite frameworks are known. SUZ-4 is a new type of synthetic zeolite [10-14]. There are some researches demonstrated and claimed that SUZ-4 has an excellent catalytic properties, high thermal stability as well as high organic solvents resistance [15-22]. However, the preparation of SUZ-4 from RHA has not been reported yet. Zeolites are normally synthesized from aqueous basic aluminosilicate precursor gels under hydrothermal conditions [23-25]. Therefore, it is very interesting to synthesize and characterize this type of zeolite under these conditions for potential applications. In this work, RHA was used as a silica source instead of silica sol. Different molar ratios of RHA and silica sol were used in order to obtain desired SUZ-4 zeolite. The synthesized SUZ-4 zeolite was characterized by X-ray powder diffraction, BET  $\text{N}_2$ -adsorption and scanning electron microscopy (SEM). This obtained SUZ-4 zeolite is expected to be used as a catalyst for reduction of  $\text{NO}_x$  and production of alcohols from greenhouse gases such as  $\text{CO}_2$  and  $\text{CH}_4$ .

## 2. MATERIALS AND METHODS

### 2.1 RHA Preparation

Dried rice husk (RH) was well washed with water and refluxed with 1 M HCl at

373 K for 3 h to remove impurities. After rinsing with water, it was dried and burned at 973 K for 1 h under oxygen flowing followed by Kongkachuichay and Lohsoontorn method [3]. The obtained white ash (RHA) was further used as natural silica source altogether with silica sol. Aluminum powder (99.7% Al, Hi Media), silica sol (LUDOX AS-40 colloidal silica, 40 wt. %  $\text{SiO}_2$ , Aldrich), tetraethylammonium hydroxide (TEAOH, 35% in water, Aldrich), potassium hydroxide (85% KOH pellet, Carlo Erba), and hydrochloric acid (37 wt.% HCl, Merck) were used as a source of alumina, silica, template, alkali and acid leaching, respectively. The TEAOH is an organic structure directing agent that can form 8-membered and 10-membered rings, which are the pore structures of a SUZ-4 zeolite.

### 2.2 SUZ-4 Synthesis

The SUZ-4 was synthesized following our previous work [25]. The starting molar ratio of used chemicals was  $7.9\text{K}_2\text{O}:\text{Al}_2\text{O}_3:21.22\text{SiO}_2:2.6\text{TEA}_2\text{O}:498.6\text{H}_2\text{O}$ . The RHA and silica sol were used as silica sources with the RHA:silica sol molar ratio of 0:100, 50:50, 70:30, 90:10 and 100:0, respectively. As a representative, the molar ratio of 50:50 is described for an example of chemical preparation. Firstly, a solution containing potassium aluminate solution was prepared by dissolving 3.54 g of KOH in distilled water, adding 0.25 g of aluminum powder and stirring continuously until the aluminum was completely dissolved forming a clear solution. The second solution containing RHA: silica sol was prepared by adjusting the molar ratio of RHA and silica sol in the range of 0 to 100 percent. The TEAOH was then added into the silica solution.

Subsequently, both solutions were mixed inside a Teflon cup and kept stirring at 500 rpm (Model M6, CAT Ingenieurbuero M. Zipperer, Germany) for 3 h. The resulting white gel with pH 13-14 was formed and then transferred to a stainless steel autoclave with 250 rpm stirring for crystallization at 423 K under autogenous pressure for 4 days. The powder product was filtered, washed with distilled water thoroughly, dried at 393 K for 2 h, and calcined at 823 K for 4 h.

### 2.3 Material Characterization

The chemical analysis of RHA silica was performed by an X-ray fluorescence (HORIBA, MESA 500-W X-ray Fluorescence Element Analyzer). The crystal structure of synthesized SUZ-4 zeolites were carried out using an X-ray powder diffraction (XRD) (Phillips, PW 1830/40) with Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The crystal morphology and size of the obtained zeolite were observed by a scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) (Jeol, JSM 5600 LV). BET specific surface area, pore size, and pore size distribution were determined using a BET-N<sub>2</sub> adsorption

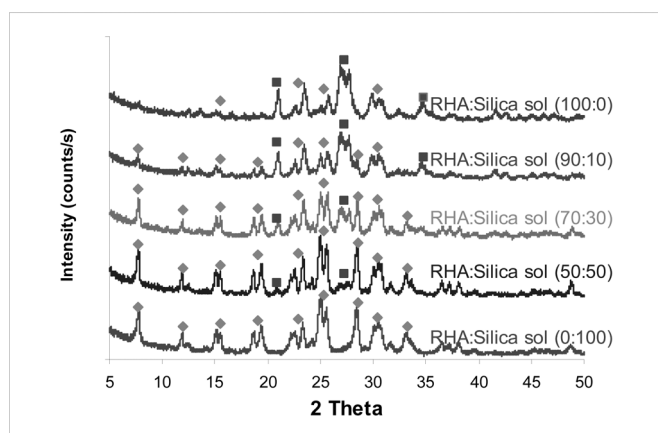
(Autosorb<sup>®</sup>-1-C, Quantachrome).

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of RHA on SUZ-4 Formation

By a mean of an XRF the prepared RHA silica was found to contain 99.7% wt. SiO<sub>2</sub> and traces of Al<sub>2</sub>O<sub>3</sub> and other metal oxides. Then it was used as a silica source for SUZ-4 zeolite synthesis under autogeneous pressure using a stainless steel autoclave at 423 K for 4 days crystallization time. The gel composition of 7.9K<sub>2</sub>O: Al<sub>2</sub>O<sub>3</sub>: 21.22SiO<sub>2</sub>: 2.6TEA<sub>2</sub>O: 498.6H<sub>2</sub>O was kept with different RHA: silica sol molar ratios (0:100, 50:50, 70:30, 90:10 and 100:0). The XRD patterns of the synthesized products having different RHA amount are presented in Figure 1. They were identified the corresponding phases by comparing to the reported standard patterns [26-28].

It is clearly shown that when the RHA was added into the silica sol the Merlinoite zeolite (MER) started to be formed. The amount of MER increased with increasing amount of RHA, based on the height of the corresponding peaks. Refer to the structure formulae of calcined MER (K<sub>11</sub>Al<sub>11</sub>Si<sub>21</sub>O<sub>64</sub>) and SUZ-4 (K<sub>x</sub>Al<sub>5</sub>Si<sub>37</sub>O<sub>72</sub>)



**Figure 1.** XRD patterns of synthesized products prepared at different RHA: silica sol molar ratios (♦SUZ-4 zeolite ■ MER zeolite).

[26-28], the Si/Al ratio of MER is 1.9 that is lower than that of SUZ-4 (Si/Al = 6.2). It implies that formation of MER requires less silica than SUZ-4. In this study, RHA was used in a solid form (average particle diameter 55 μm) while the silica sol was in a form of colloidal solution. Thus, the RHA required longer time to be dissolved completely to form silicate unit ( $[\text{SiO}]^+$ ), the primary unit of 3-D structure of zeolite, compared to the higher active silica sol. Moreover, zeolite crystallization is a competitive reaction which depends on the conditions of the set up system and nature of each involving chemical species. Therefore, when RHA was used the availability of silicate unit was quite limited and favored the formation of MER instead of SUZ-4. This result is in well agreement with Gujar *et al.* [17] who reported that the SUZ-4 formation was occurred in narrow range conditions and was very sensitive to various factors.

### 3.2 Product Characterization

The SEM micrographs of the products were taken as shown in Figure 2. The pictures confirm the formation of SUZ-4 as needle-shape crystals and MER as oval-shape crystals. The amount of MER presented in the pictures conforms to the XRD results, which is varied with the amount of RHA used. By using an image analyzing software (ImageJ) on the SEM micrographs (Figure 2), it is evident that the crystal of SUZ-4 was enlarged from approximately  $0.07 \pm 0.02 \times 1.7 \pm 0.2 \mu\text{m}$  (Figure 2a) to  $0.2 \pm 0.01 \times 5.0 \pm 1.5 \mu\text{m}$  (Figure 2b) and (Figure 2c). However, when RHA was used at 90 % and 100 % the SUZ-4 crystal was shrunk to  $0.13 \pm 0.01 \times 2.8 \pm 0.2 \mu\text{m}$  (Figure 2d) and  $0.09 \pm 0.04 \times 2 \pm 0.2 \mu\text{m}$  (Figure 2e), respectively. This decrease was influenced by the formation of the competing MER, which is also consistent with the XRD results.

Nitrogen adsorption-desorption

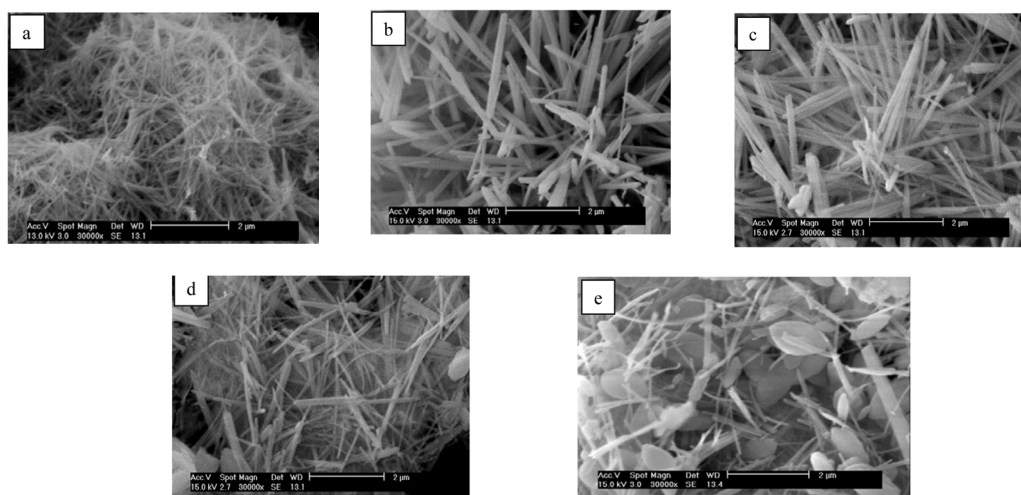
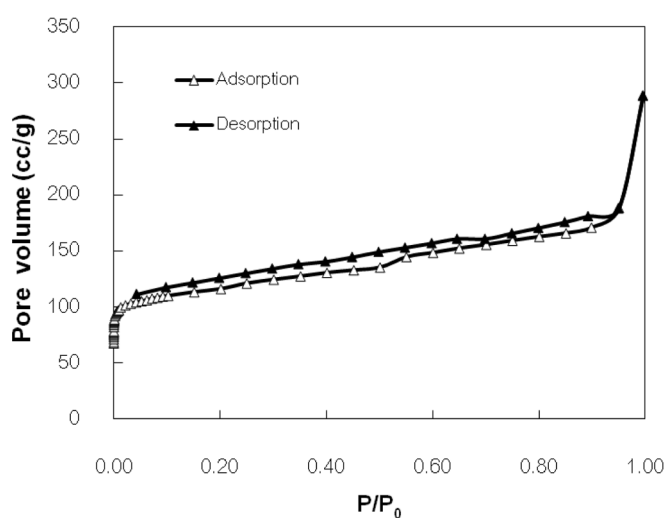


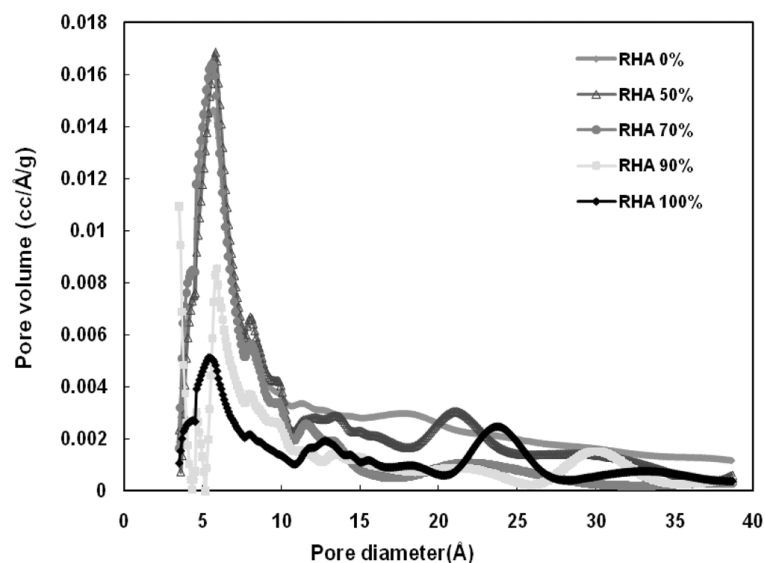
Figure 2. SEM micrographs of as-synthesized SUZ-4 from different molar ratios of RHA: silica sol (a) 0:100 (b) 50:50 (c) 70:30 (d) 90:10 (e) 100:0.

isotherms of calcined samples were measured at 77 K while the degassing temperature was carried at 523 K. They all revealed the type A hysteresis that corresponds to cylindrical-shape pores. Figure 3 shows a typical isotherm obtained from the product prepared by using 50 % RHA.

Additionally, Figure 4 illustrates the pore size distribution curves of SUZ-4 with different amount of RHA used. With 100 % silica sol, the pore size of the obtained SUZ-4 exhibits almost mono-distribution having the main peak that has a mean size at approximately 5.6 Å and a small shoulder at approximately 4.4 Å. This is



**Figure 3.** N<sub>2</sub> adsorption (open symbols) and desorption (solid symbols) isotherms of SUZ-4 (RHA: silica sol = 50:50).



**Figure 4.** Pore size distribution of as-synthesized SUZ-4 zeolite from different mole percentages of RHA.

corresponded to the sizes of two types of channels comprising 10-membered ring and 8-membered ring, respectively [11]. When the RHA was used together with the silica sol, according to the evidences from XRD and SEM micrographs, the more RHA used the lesser amount SUZ-4 was formed and also the lower peak height at 4.4 and 5.6 Å. The detected pores with the sizes larger than 5.6 Å should be the voids created among the crystals. These voids seem to be enhanced by the coexistence of SUZ-4 and MER phases.

Accompanied with pore size distribu-

tion, the surface area and the micropore volume as well as total pore volume of the products were also analyzed and summarized in Table 1. The result clearly shows that the surface area and pore volume are directly related to the amount of SUZ-4 formed. With 50 % RHA, high purity of SUZ-4 was obtained having the same surface area ( $\sim 247 \text{ m}^2/\text{g}$ ) as that of 100 % silica sol. With 70 % RHA and above, the surface area and pore volume drastically decrease by 61% and 76%, respectively, as the result of coexistence of MER phase.

**Table 1.** Surface areas, micropore volume and total pore volume of obtained zeolites.

RHA:silica sol	Specific surface area <sup>a</sup> (m <sup>2</sup> /g)	Micropore volume <sup>a</sup> (cm <sup>3</sup> /g)	Total pore volume <sup>b</sup> (cm <sup>3</sup> /g)
0:100	247.4	0.1510	0.8114
50:50	247.2	0.0795	0.4469
70:30	186.2	0.0722	0.3224
90:10	126.5	0.0225	0.1902
100:0	97.16	0.0017	0.1975

<sup>a</sup> t-plot micropore analysis method

<sup>b</sup> MP micropore analysis method

#### 4. CONCLUSIONS

SUZ-4 zeolite was successfully synthesized from RHA silica under autogenous pressure using a stainless steel autoclave at 423 K for 4 days crystallization time with TEAOH as a structure directing agent. As a result, the amount of Merlinoite zeolite (MER) phase increased with increasing amount of RHA used. The differences in crystal size, specific surface areas, pore volume, and pore size distribution have been reported. With 50% RHA, high purity of SUZ-4 was

obtained having the same surface area ( $\sim 247 \text{ m}^2/\text{g}$ ) as that of 100 % silica sol. The SUZ-4 crystal size was shrunk when 90 % and 100 % RHA were used due to the influence from the formation of MER.

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