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Synthesis of ZSM-5 zeolite and silicalite from rice husk ash

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ABSTRACT

Local rice husk was precleaned and properly heat treated to produce high purity amorphous SiO_2 for use in the synthesis of ZSM-5 zeolite and silicalite by hydrothermal treatment (150 °C) of the precursor gels (pH 11) under autogenous pressure in a short reaction time (4–24 h). A wide range of SiO_2/Al_2O_3 molar ratios (30–2075) and a small template content were employed to fully exploit the potential of rice husk ash (RHA). The mineralogical phases, morphology, specific surface area and pore volume of the synthesized products were investigated by XRD, FT-IR, SEM and BET analyses, respectively. Under the employed conditions, it was found that the gels with a low range of SiO_2/Al_2O_3 molar ratios (<80) produced an amorphous phase to poorly crystalline ZSM-5 zeolite; those with a medium range (80–200) favored well crystalline ZSM-5 zeolite production with a large surface area; whilst those with a high range of SiO_2/Al_2O_3 molar ratios (>200) yielded silicalite. The increase in Na_2O content, which was derived from the addition of $NaAlO_2$ to attain the desired SiO_2/Al_2O_3 molar ratio of the gel, did not significantly enhance the crystallization rate, crystallinity, or yield of products. On the contrary, these properties were greatly affected by the increase in the SiO_2/Al_2O_3 molar ratio.

1. Introduction

Rice husk ash (RHA) is a solid waste product from the power generating industry which is suitable for recycling. The silica in rice husk is amorphous and transforms to crystalline silica when it is heated at high temperatures. The transformation temperature is affected by its chemical purity and particle size. In Thailand an enormous quantity of industrial waste grade RHA has been produced which directly affects upon the environment and imposes adequate storage problems and concerns. The International Agency for Research on Cancer (IARC) announced in 1997 that crystalline silica forms, such as quartz and cristobalite, belong to "Group 1" of hazardous materials which is the same group as asbestos. Accordingly, respirable crystalline silica is recognized as a material that can cause respiratory and other tissue damage including of cancer. To protect the environment and decrease the amount of RHA waste products requiring contained storage, finding an appropriate utilization of the ash is essential. It has been known that SiO_2 in industrial waste RHA can exist in both amorphous and crystalline (mostly cristobalite) forms depending on its heat treatment history, or, more precisely, the operating temperature characteristics of the boiler. The suspension type boilers produce mostly amorphous SiO_2 whilst the Stoker types produce mostly cristobalite. Therefore, industrial waste RHA is a potentially attractive source for the large scale production of ZSM-5.

In addition to environmental and operative safety concerns, to be economically able to compete with established commercial ZSM-5 production, a simple and low cost production route has to be employed. Apart from the use of a low temperature hydrothermal reaction under autogenous pressure of the aqueous suspension, using a low cost but abundant and renewable source of SiO_2 with high potential, i.e. fine grain, high porosity, large surface area, high purity and in an amorphous form, is promising since the crystallization time can be greatly reduced and a high yield attained. According to Mosungnoen and Wada [1], the amount of amorphous silica in Thai rice husk is about 20% (w/w). The ash from the unwashed husk contains about 96% (w/w) silica and some amount of organics, alkali oxide, and impurities but, with an appropriate washing of the husk, the ash can contain >99% (w/w) silica. The alkalis, especially K_2O and Na_2O, in the rice husk accelerate the transformation of amorphous SiO_2 to cristobalite or tridymite with a reduction in the transformation temperature from ~1200 °C in the absence of alkali to ~800 °C at low alkali contents (<1%, w/w).

Although there have been many research documents encouraging the utilization of SiO_2 from RHA for the synthesis

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Table 1
Initial chemical compositions of the precursor gels.

SiO_2/Al_2O_3	Na_2O[a]$/SiO_2$	$NaAlO_2$ (mg)	H_2O (g)	NaOH (mg)	TPABr (g)	RHA (g)
30	0.212	209.8	49.2	424	0.5	2
50	0.194	124.7	49.2	424	0.5	2
80	0.182	76.8	49.2	424	0.5	2
100	0.177	60.8	49.2	424	0.5	2
200	0.169	28.9	49.2	424	0.5	2
400	0.165	13.1	49.2	424	0.5	2
800	0.163	4.9	49.2	424	0.5	2
1000	0.162	3.3	49.2	424	0.5	2
2075	0.160	–	49.2	424	0.5	2

[a] Total Na_2O.

Table 2
The chemical analysis (XRF) and BET surface area of RHA silica.

Chemical composition	wt%
SiO_2	99.64
Al_2O_3	0.08
K_2O	0.04
Na_2O	0.00
P_2O_5	0.10
CaO	0.04
SO_3	0.03
Fe_2O_3	0.04
CuO	0.01
MoO_3	0.01
Others	0.03

SiO_2/Al_2O_3 molar ratio = 2075. Average particle size (SEM) of the ground RHA silica ~0.1 μm.

of various types of zeolite [2–4], the reported experimental results so far are equivocal in their potential suitability and optimal methods for utilization, due in part to the differences in the nature of the ‘as-prepared RHA’ and in the composition of the precursor gel. This hence leaves room for further refinements. As a part of a full-scale study on the viability of the synthesis method adopted by our research team, the following experimental results are presented: pretreatment of the rice husk and the effect of the SiO_2/Al_2O_3 molar ratio on the crystallization rate, the crystallinity and stability of the zeolite. A locally obtained source of RHA was collected, washed first with water, and then with dilute HCl to reduce the alkali content, prior to burning of the ash. In the present study, we have performed a hydrothermal synthesis (150 °C) of a highly siliceous zeolite, of the type ZSM-5, under autogenous pressure, using a wide range of SiO_2/Al_2O_3 molar ratios, starting from 30 up to 2075, the latter limit of which is the original ratio of the RHA silica.

2. Experimental

2.1. Materials

RHA silica was prepared by burning the acid leached rice husk [5] at 700 °C for 3 h followed by sieving through a mesh number 230 screen (as-prepared RHA silica, BET surface area = 240 m^2/g) and grinding to fine powder in a pulverizer. The obtained white ash, as agglomerates of ground RHA silica, with a SiO_2/Al_2O_3 molar ratio of 2075, consisted of amorphous SiO_2. Sodium aluminate ($NaAlO_2$ powder, Riedel-de Haën), tetrapropylammonium bromide (TPABr powder, Merck), sodium hydroxide (NaOH pellets, Merck) and nitric acid (AnalaR) were used as source of alumina, template, alkali and pH regulator, respectively.

2.2. Methods

The hydrothermal synthesis of ZSM-5 zeolite was performed in a stainless steel bomb lined with PTFE under autogenous pressure at different SiO_2/Al_2O_3 molar ratios, from the as-prepared ground RHA silica, under hydrolysis at 150 °C for 48 h, using a low concentration of TPABr as the organic template. The preparation of the precursor gels was performed by a modification to that of Mohamed et al. [6]. Briefly; 2.0000 g finely ground RHA silica and 0.18 mol/L TPABr solution were mixed with 0.27 mol/L NaOH solution in a final volume of 50 mL and the resultant suspension was stirred for 30 min at room temperature. An aqueous solution of sodium aluminate was prepared separately by mixing a calculated proportion of sodium aluminate and 0.27 mol/L NaOH solution to obtain the gel with a desired SiO_2/Al_2O_3 molar ratio (Table 1). The sodium aluminate solution was then added to the suspension with stirring for 1 h at room temperature. The pH of the gel was adjusted to about 11 by the addition of 1 mol/L HNO_3 acid before hydrothermal treatment at 150 °C. After each time interval, the obtained product was separated by centrifugation, washed with distilled water, dried at 80 °C for 12 h and calcined in air at 550 °C for 5 h to remove the organic template, cooled in desiccators and then weighed to four decimal places. The weight obtained based on the weight of the ground RHA silica plus Al_2O_3 (in the $NaAlO_2$ powder) was taken as the product yield (wt%) [7].

2.3. Characterization

The chemical analysis of the RHA silica was performed by X-ray fluorescence (XRF) with a Philips PW 1480 spectrometer. The

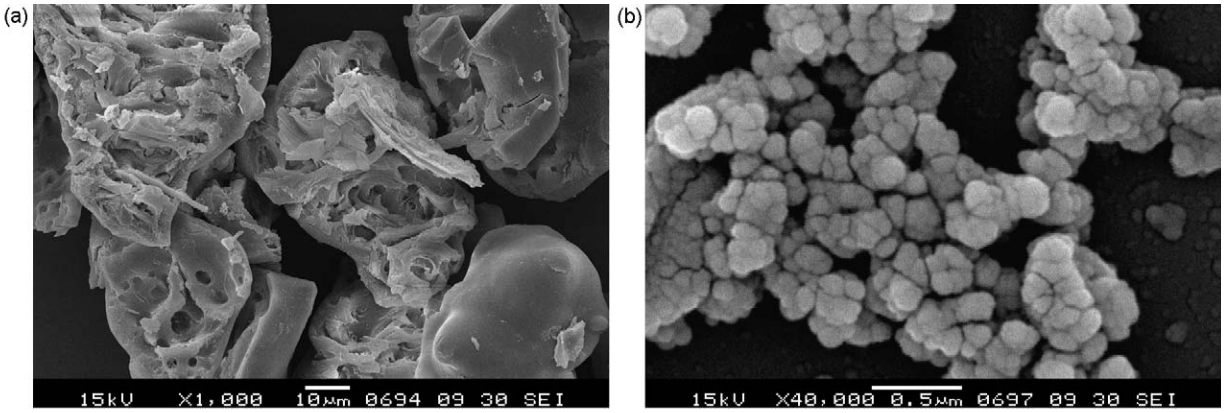

Fig. 1. Representative SEM micrographs of (a) as-prepared RHA silica grains and (b) agglomerates of ground RHA silica.