UTILIZATION OF RICE HUSK AS RAW MATERIAL IN SYNTHESIS OF MESOPOROUS SILICATES MCM-41

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ABSTRACT

The research about synthesis and characterization of MCM-41 from rice husk has been done. Silica (SiO_2) was extracted from rice husk by refluxing with 3M hydrochloric solution at 80 °C for 3 h. The acid-leached rice husk was filtered, washed, dried and calcined at 650 °C for 6 h lead the rough powder of rice husk silica with light brown in color. Characterization was carried out by X-ray diffraction (XRD) and FTIR spectroscopy method. Rice husk silica was dissolved into the sodium hydroxide solution leading to the solution of sodium silicate, and used as silica source for the synthesis of MCM-41. MCM-41 was synthesized by hydrothermal process to the mixture prepared from 29 g of distilled water, 8.67 g of cetyltrimethyl ammonium bromide (CTMAB), 9.31 g of sodium silicate solution, and amount mL of 1 M H_2SO_4. Hydrothermal process was carried out at 100 °C in a teflon-lined stainless steel autoclave heated in the oven for 36 h. The solid phase was filtered, then washed with deionised water, and dried in the oven at 100 °C for 2 h. The surfactant CTMAB was removed by calcination at 550 °C for 10 h with heating rate 2 °C/min. The as-synthesized and calcined crystals were characterized by using FTIR spectroscopy, X-ray diffraction and N_2 physisorption methods. In order to investigate the effect of silica source, the same procedure was carried out by using pure sodium silicate as silica source. It was concluded that silica extracted from rice husk can be used as raw materials in the synthesis of MCM-41, there is no significant difference in crystallinity and pore properties when was compared to material produced from commercial sodium silicate.

Keywords: *MCM-41, rice husk, silica*

INTRODUCTION

Indonesia is one of the major countries in the rice producing, whereby it generates abundance of waste known as rice husk, a thin but abrasive skin in nature covering the edible rice kernel. About 20% of the rice husk ash residues left after the combustion cause environmental problems due to the pollution of both water and air. On the other hand, rice husk can be considered as a useful matter, which can be employed as raw materials in kinds of applications [1-3]. The rice husk is largely composed of silica with small amounts of inorganic compounds. Previous research had shown that pure silica can be obtained from rice husk by an acid-leaching procedure and calcination at 600 °C under atmosphere pressure. HCl is most often used for acid leaching [4-5]. The extraction of silica from rice husk by acid treatment provides more than 95% by weight of amorphous silica [2,6].

MCM-41 is amorphous material consists of uniformly and highly ordered network of silica with unidimensional and hexagonally shaped. The pore size of the MCM-41 can be controlled from 2 to 10 nm by use of an appropriate surfactant as a template [5]. These outstanding characteristics such as high surface area and high thermal stability results in various applications of MCM-41. For examples, it can be used as a catalyst itself or being a catalyst support as well as an ion exchanger [5,7]. MCM-41 was prepared originally by hydrothermal reactions of silicate gels in the temperature range from 100-120 °C [5].

The pure silicate substances such as sodium silicate and tetra ethyl ortho silicate (TEOS) usually were used as a silica source in the synthesis of MCM-41. Due to its high silica content rice husk has become a source for preparation a number of silicon compounds such as mesoporous MCM-41[7]. By using rice husk as the silica source in the synthesis of MCM-41, the production costs can be reduced subsequently besides helping to overcome environmental pollution.

From such viewpoints, here the authors report the utilization of rice husk as source of silica in the synthesis of mesoporous silicates MCM-41. The product (denoted as RH-MCM-41) was characterized by XRD, FTIR and physisorption methods, and compared to MCM-41 synthesized from commercial sodium silicate by the same procedure (denoted as Si-MCM-41). The results showed that rice husk can be used as raw material in the synthesis of MCM-41. The crystallinity characterization and the pore properties of

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MCM-41 synthesized from rice husk were similar to those of MCM-41 synthesized from commercial sodium silicate.

EXPERIMENTAL SECTION

Materials

The materials used for the preparation of the mesoporous silicates MCM-41 were: rice husk found from some rice huller industries in Bantul, Yogyakarta, Indonesia, sodium silicate (27% (wt) SiO_2, 8% (wt) Na_2O, 65% (wt) H_2O), hydrochloric acid (HCl), cetyltrimethyl ammonium bromide (CTMAB), sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), and distilled water produced by Laboratory of Basic Chemistry Universitas Gadjah Mada Yogyakarta, Indonesia.

Instrumentation

The equipments used in this research included chemical laboratory glassware, 3X Shimadzu X-ray diffractometer (XRD) with Cu-Kα radiation, and PC-8201 Shimadzu Fourier Transform Infrared (FTIR) Spectrometer and NOVA Ver. 2.00 sorptiometer.

Procedure

Preparation of silica from rice husk and characterization

The rice husk was washed thoroughly with water to remove adhering dust and soil, and then dried at 120 °C overnight. The water rinsed rice husk (100 g) and 500 mL of 3 M HCl solution were refluxed under stirring in a round-bottomed flask at 80 °C for 3 h. The mixture was filtered and the husk was washed with distilled water several times until the filtrate was free from acid. The acid-leached husk was then dried at 120 °C overnight and calcined at 650 °C for 6 h, with a heating rate of 2 °C/min. The silica from rice husk was characterized by FTIR and XRD method.

Synthesis of sodium silicate solution

The solution of sodium silicate (Na_2SiO_3) was prepared by mixing 4.0 g of rice husk silica with 1.25 g of NaOH pellet and 35 g of distilled water. The resulting gel mixture was heated and stirred for 2 h at 353 K. The mixture was then cooled to room temperature.

Synthesis of RH-MCM-41 and Si-MCM-41

RH-MCM-41 was synthesised by hydrothermal method as follows. CTMAB (8.67 g) and 29 g of distilled water were mixed and stirred for 30 min. There after 9.31 g of sodium silicate solution prepared from rice husk silica was added dropped wise to the surfactant solution under vigorous stirring. After stirring for 30 min a small amount of 1 M H_2SO_4 was added to those mixtures to reduce the pH to 10.2 and stirred for 1 h. The silica-surfactant gel found was hydrothermally treatment at 110 °C in a teflon-lined stainless steel autoclave for 36 h. After cooling at the room temperature, the resulting solid product was recovered by filtration on a Buchner funnel, washed with distilled water, and dried in the open air at 90 °C. Surfactant was removed by calcining the as-synthesized product at 550 °C for 10 h with heating rate of 2°/min. In order to investigate the effect of silica source, the same procedure was carried out by using commercial sodium silicate leading to Si-MCM-41.

Characterization

Characterization of the powder phases and determination of the phase purities in the calcined MCM-41 samples were carried out by XRD (Shimadzu XD-3H) using nickel-filtered Cu K_α radiation (λ = 1.5406 Å). The samples were scanned from 1 to 10° (2θ), where θ is the angle of incidence of the X-ray beam to the plane. The lattice parameter (a0) was calculated by formula: $a_0 = 2d_{100}/\sqrt{3}$, where d_{100} is the interplanar spacing corresponding to the (100) Bragg reflection. Infra-red spectra were recorded with a Shimadzu-8201 PC FTIR Spectrometer from KBr Pellets (0.005 g sample with 0.1 g KBr). The specific surface area and pore diameter of calcined-MCM-41 were analyzed using a NOVA Ver. 2.2 sorptiometer, by apply the conventional Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) equations. The pore wall thickness was calculated by subtracting the pore diameter from the lattice parameter (a_0).

RESULT AND DISCUSSION

Characterization of Silica prepared from rice husk

Sample of silica extracted from rice husk was rough powder with light brown in color. The FTIR spectrum of sample was presented in Fig. 1, that shows an intense asymmetric, symmetric stretching and bending vibration for Si-O-Si bonds at wave numbers 1110, 798, and 478 cm^{-1} respectively [8]; whereas the absorption band at around 3425 cm^{-1} related to left water molecule [8]. The absorption band at around 960 cm^{-1} is not detected. It reveals that there is no silanol group.

Fig. 2 shows the XRD diffractogram of the sample in the range of 2θ = 20-80°. There is no peak, except the broad hump around 2θ = 23°, indicates that the rice husk silica is in amorphous phase [3].

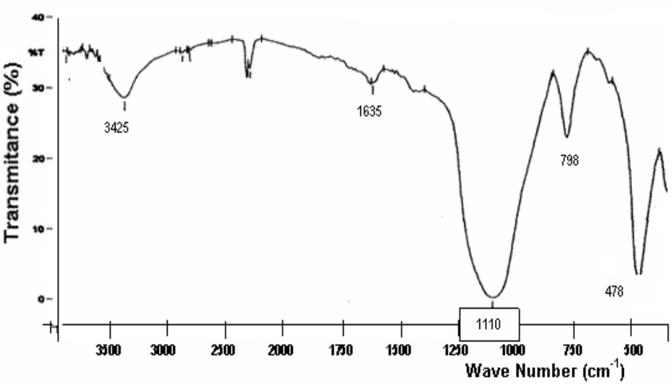


Fig 1. FTIR spectra of silica extracted from rice husk

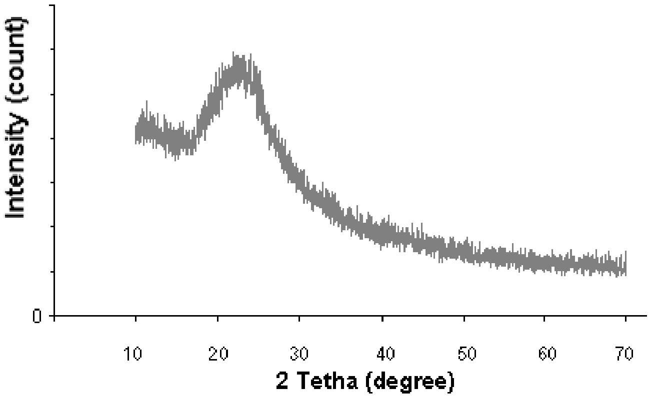


Fig 2. Diffractogram of silica prepared from rice husk

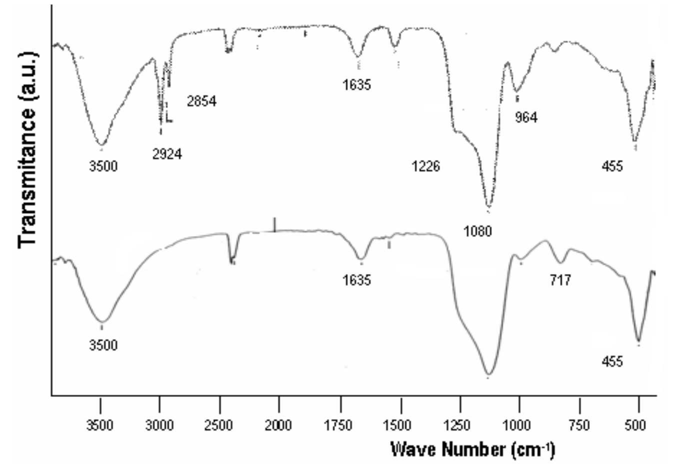


Fig 3. FTIR spectra of RH-MCM-41: as-synthesized (A) and calcined (B)

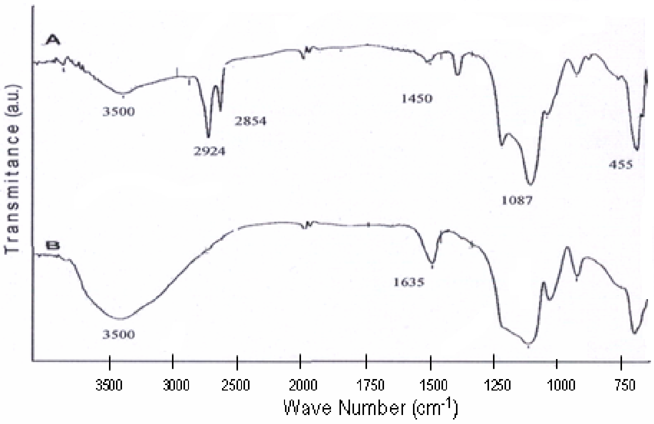


Fig 4. FTIR spectra of Si-MCM-41: (A) as-synthesized and (B) calcined

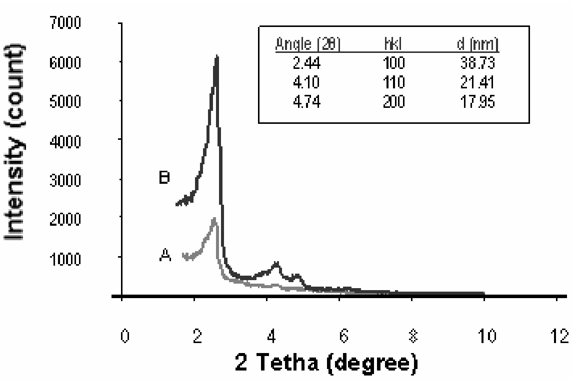
Characterization of MCM-41

FTIR Spectra

Shown in Fig. 3 and Fig. 4 are the FTIR spectra of RH-MCM-41 and Si-MCM-41 respectively before and after calcination in the wavenumber region of 400-4000 cm^{-1}. No significant difference was observed in the structure of RH-MCM-41 and Si-MCM-41.

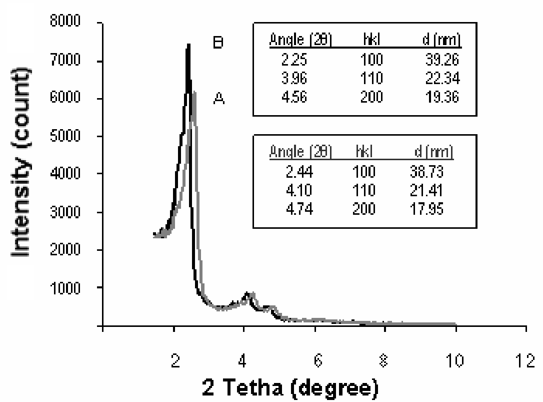
The as-synthesized MCM-41 sample on both figures shows well defined bands at about 2924 and 2854 cm^{-1} corresponding to *n*-C-H and *d*-C-H stretching vibration of surfactant molecules [8]. The broad bands around 3500 cm^{-1} attributed to the silanols at the external surface and adsorbed water molecules, while deformational vibrations of adsorbed molecules cause the absorption bands at around 1635 cm^{-1}. The band at 717 cm^{-1} is associated with vibrations by the organic template [8].

Based on the spectrum of calcined samples, both of spectra exhibit sharp bands around 1080 cm^{-1} and 1226 cm^{-1} of wave number which characteristic for vibration of symmetric and asymmetric stretching O-Si-O bridge respectively [8]. These bridges are the part of silicates polymer formed in the hydrothermal treatment [9]. A broad absorption band in the hydroxyl region between 3000 and 3700 cm^{-1} with a maximum in the range of 3450-3500 cm^{-1} was observed in both cases. This band associated with stretching vibration of Si-O-H group in the framework perturbed by physically adsorbed water molecules [8]. Due to the emerge of a lot of Si-O-H groups after calcination, the intensity of those absorption band was significantly increased. The band at around 964 cm^{-1} is associated with symmetric Si-O-H stretching vibration, while the band at around 455 cm^{-1} is assigned to a SiO_4 bending mode. There is no an absorption bands at 2924 and 2854 cm^{-1} assigned asymmetric and symmetric stretching vibration of $-CH_2-$, respectively; attributed to the perfectly combustion of surfactant in the calcination treatment. Those bands indicated that the RH-MCM-41 and Si-MCM-41 was successfully synthesized.



Angle (2θ)	hkl	d (nm)
2.44	100	38.73
4.10	110	21.41
4.74	200	17.95

Fig 5. XRD patterns of RH-MCM-41: (A) as-synthesized and (B) calcined-MCM-41



Angle (2θ)	hkl	d (nm)
2.25	100	39.26
3.96	110	22.34
4.56	200	19.36

Angle (2θ)	hkl	d (nm)
2.44	100	38.73
4.10	110	21.41
4.74	200	17.95

Fig 6. XRD patterns of calcined-RH-MCM-41 (A) and calcined-Si-MCM-41 (B)

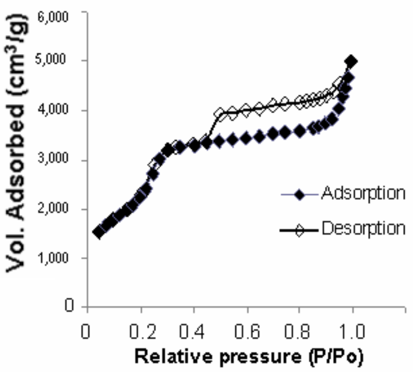


Fig 7. Nitrogen absorption-desorption isotherms of RH-MCM-41

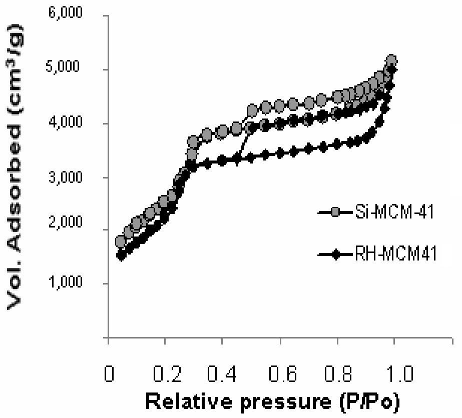


Fig 8. Nitrogen adsorption-desorption isotherms of calcined-RH-MCM-41 and Si-MCM-41

X-ray Diffractogram

Fig. 5 shows the XRD patterns of as-synthesized and calcined-RH-MCM-41. It is seen that the calcined-RH-MCM-41 diffractogram exhibits three peaks which can be indexed as 100, 110, and 200 plane respectively; and 44.71 Å of lattice parameter, a_0 (calculated by formula: $a_0 = 2d_{100}/\sqrt{3}$). It was in good agreement with MCM-41 diffractogram reported by some previous reseachers. The diffractogram of MCM-41 published by Beck et al. [5] displayed 4 peaks with 100, 110, 200, and 210 of Miller Index and 45 Å of lattice parameter. Whereas Kresge et al. [8] reported MCM-41 diffractogram with 100, 110, 200, and 210 of Miller Index and 40 Å of lattice parameter. The main peak at 2-3° of 2θ assigned the ordered hexagonal structure of MCM-41, while the other weak peaks at 4-6° of 2θ attributed the highly ordered of the structure [5,10].

Upon calcination in the air at 823 K for 10 h with heating rate 2°/min., the intensity of the XRD peaks increased by about 3 times compared to the as-synthesized RH-MCM-41. These results reflect that the degree of ordering was dramatically improved by surfactant removal. In addition, after calcination 2θ of the main peak shifts to a higher value (25.4° for as-synthesized sample and 26° for calcined sample), indicating contraction of the lattice. Contraction of the lattice is caused by the removal of template and subsequent condensation of silanol (Si-OH) groups.

In Fig. 6 the XRD patterns of calcined-RH-MCM-41 and calcined-Si-MCM-41 are compared. That figure shows the little dependence of quality of MCM-41 on the silica sources used. High quality of MCM-41 was produced from both RHA and commercial silica. XRD of Si-MCM-41 shows a slightly higher in resolution and intensity resulted from slightly higher crystallinity than that of RH-MCM-41. In addition, the calcined-RH-MCM-41 shows a higher value in 2θ of the peak, indicated that the sample has thinner in pore walls compared to Si-MCM-41. It seems the purer commercial silica can polymerize by more perfectly than RH in the formation of pore walls.

Nitrogen physisorption

Fig. 7 shows the nitrogen adsorption-desorption isotherms of RH-MCM-41. According to IUPAC classification, type IV isotherms are obtained for this material. It can be observed that a well-defined step occurs in the adsorption curve at a relative pressure

Table 1. The pore properties of the sample

Sample	Specific surface area, S_{BET}, (m^2/g)	Mean pore diameter, d_{mp} (nm)	Latice parameter, a_o (nm)	Pore walls thickness, W_t (nm)
RH-MCM-41 (prepared from rice husk silica)	903.423	3.276	4.414	1.138
Si-MCM-41 (prepared from commercial silica)	946.607	3.357	4.533	1.176
RH-MCM-41 reported by Siriluk and Yuttapong (2005)	730	2.2	*)	*)

*) Not reported

$P/P0$ of 0.2-0.3 indicating the filling of framework-confined mesopores. The pore filling (by capillary condensation) for that sample is restricted to a narrow range of $P/P0$ = 0.2-0.3, which is a typical feature for mesoporous MCM-41 materials [11]. These results coincide with the results of XRD patterns.

This isotherm exhibits three stages; the first stage was a linear part going through the origin, which was caused by monolayer absorption of N_2 on the walls of the mesopores ($P/P_0 < 0.20$). The second stage was at higher pressures, which the absorption in mesopores leads to multilayer formation until condensation takes place, giving a sharp increase in absorption volume. According to Zhao et al. [11] and Selvam et al. [12], the P/P_0 value at which the inflection starts (at ca. P/P_0 = 0.20) is attributed to the commencement of pore filling from which the pore diameter can be roughly estimated. The sharpness in this step indicates the uniformity of the pore size distribution. As the mesopores are filled, the absorption continues on the external surface. The third stage in the absorption isotherm was an almost horizontal part after the relative pressure P/P_0 of ± 0.35, due to multi layer absorption on the outer surface of the particles [11,13]. The total mesopore volume was calculated from the amount of vapor adsorbed at P/P_0 = 0.35; assuming that MCM-41 were then filled with condensed liquid nitrogen in the normal liquid state.

The hysteresis loop is observed at relative pressure P/P_0 of > 0.42. It is consistent with type H3 hysteresis and is characteristic of capillary condensation between lamellar particles or in solids containing slit-shaped mesopores. According to Gusev et al. [14] there are two possible explanations: condensation of the nitrogen (a) in interparticle spaces and/or (b) in residual lamellar mesostructures which occur during the templating mechanism which forms the hexagonal structure. The absence of hysteresis loops in the capillary condensation range is an indication that the material possesses pores in a lower mesopore range [15].

In Fig. 8 the nitrogen adsorption-desorption isotherms of calcined-RH-MCM-41 and Si-MCM-41 are compared. It could be observed that both of samples have similar in nitrogen adsorption-desorption curves. Due to its smaller in adsorption capacities, the isotherm of RH-MCM-41 gives lower adsorption values over the whole relative pressure range. For the Si-MCM-41, the adsorption step corresponding to nitrogen condensation in primary mesopores is shifted toward higher relative pressure indicating the occurrence of larger pores in this material in compared to RH-MCM-41. With increasing pores size the occurrence of pore condensation is shifted to higher relative pressures as expected from classical theories of pore condensation. The knees for RH-MCM-41 isotherm are not as steep as that of Si-MCM-41. According to Zhao and Lu [11], it is reflecting that the first sample has a relatively broader in pore size distribution than the other one.

The pore properties of RH-MCM-41 and Si-MCM-41 in this research and RH-MCM-41 reported by Siriluk and Yuttapong [7] were presented in Table 1.

The specific surface area (S_{BET}) was determined by using Brunauer-Emmett-Teller equations from the linear section of the BET plot, i.e. in the relative pressure range (0.05-0.25). The mean pore diameter (d_{mp}) was calculated from the N_2 adsorption data, using the BJH (Barrett-Joyner-Halenda) method. The latice parameters (a_0) were calculated by formula: $a_0 = 2d_{100}/\sqrt{3}$, where d_{100} is the interplanar spacing corresponding to the (100) Bragg reflection. The wall thickness (W_t) is calculated by subtracting the pore diameter from the lattice parameter (a_0). According to Table 1, there is no significant difference was observed in the pore properties of MCM-41 prepared from RH and commercial silica in this research. RH-MCM-41 produced in this research has larger both in specific surface area and mean pore diameter than that of similar material reported by Siriluk and Yuttapong [7].

CONCLUSION

Silica prepared from rice husk can be used as raw materials in the synthesis of MCM-41. The pore properties of the product are: 903.423 m^2/g of specific surface area (S_{BET}), 3.276 nm of mean pore diameter (d_{mp}), 3.276 nm of lattice parameter (a_0), and 3.276 nm of pore walls thickness (W_t). There is no significant difference in crystallinity and pore properties when was compared to material produced from pure sodium silicate.

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