

Structure of Mesoporous MCM-41 Prepared from Rice Husk Ash

C. Siriluk and S. Yuttapong

*Division of Environmental Technology, School of Energy and Materials
King Mongkut's University of Technology Thonburi
Bangkok, Thailand. Siriluk.Chi@kmutt.ac.th*

Corresponding author C. Siriluk

Abstract

Mesoporous silicate particles, called MCM-41 were produced from rice husk ash generated by a biomass fired power plant. More than 95 % of amorphous silica was extracted from rice husk ash by acid leaching. The RHA_MCM-41 particles were synthesized using sodium silicate prepared from rice husk ash and commercial sodium silicate as a silica source and hexadecyltrimethylammonium bromide (CTAB) as an organic template. The mixture was stirred at room temperature for 48 h and then calcined at 550 °C for 4 h. The crystallinity characteristics and the porosity properties of MCM-41 synthesized from rice husk ash were similar to those of MCM-41 synthesized from commercial silica. The results from the X-ray diffraction (XRD) indicated the well-defined crystallinity of the synthesized MCM-41. The diameters determined from the Scanning Electron Micrographs of fine silica particles and the MCM-41 particles were approximately 50 μm and 0.3-0.5 μm , respectively. The images from Transmission Electron Microscope (TEM) of the MCM-41 particles confirmed the arrangement of hexagonal patterns, which is the distinctive characteristic of M41S families. The Brunauer-Emmett-Teller (BET) surface area of the RHA_MCM-41 particles determined from nitrogen adsorption isotherm was about 730 m^2g^{-1} and its pore sizes estimated from the TEM images agreed very well with the pore sizes calculated from the data of nitrogen isotherms. The plots of pore size distributions using the Barret-Joyner-Halenda (BJH) method showed quite narrow pore diameter distributions, centered around 2.2 nm, corresponding to the TEM results.

Keyword: MCM-41, rice husk ash, silica

1. Introduction

Rice husk is a by-product from rice mill that was used as an energy source in many industries such as biomass power plant and rice mill. Burning rice husk generates rice husk ash (RHA) which is rich in silica and can be an economically valuable raw material for production of natural silica [1].

There are several methods for the extraction of silica from biomass. Many authors [2,3,4,5], have suggested that acid preliminary treatment before thermal treatment is a reasonable method for natural silica extraction. The high purity of silica and low mineral impurity are retrieved by boiling in hydrochloric solution for 1 h followed by burning in the atmosphere at 650-700 °C for 4 h [3]. By means of this method, the extracted silica is found in a form of amorphous structure which is the most reactive form for silylation reaction.

Since mobile corporation have discovered nanostructured mesoporous materials known as M41S in the late 1980s [6], MCM-41, one of the M41S family, has become the best known and most interesting material. Due to its excellent properties such as high surface area, well defined regular pore shape, narrow pore size distribution, large pore volume, tunable pore size and thermal stability, MCM-41 has been utilized for chemical and environmental applications such as an adsorbent, catalyst support, ion-exchanged material and nanofilter [7]. The MCM-41 particles are generally synthesized from various silica sources; sodium silicate, fumed silica or tetraethylorthosilicate (TEOS) and alkali surfactant solutions (C12-C18) as a template [8,9]. Thus, silica source from rice husk ash would be an alternative for the synthesis of MCM-41. This benefit is not only to reduce the amount of ash waste but also to enhance the ash value.

In this study, MCM-41 was prepared by using silica extracted from the rice husk ash. The chemical and physical properties characterized by means of crystallinity, porosity and surface study was then compared with those of MCM-41 synthesized from commercial sodium silicate.

2. Experimental

2.1 Silica Extraction

Raw material used for the experiment was rice husk ash (fly ash) produced by the process of fluidized bed gasification from a biomass power plant located in Chainat province, Thailand. Rice husk ash was boiled in 1 M HCl at 80 °C for 1 h. After acid pretreatment, the ash was rinsed with distilled water, dried in an oven at 110 °C overnight and then calcined in a muffle furnace at 650 °C for 4 h. The crystallinity and mineral composition of the extracted silica were examined by XRD and XRF techniques, respectively. Then, the extracted silica was utilized as a siliceous raw material for MCM-41 preparation.

2.2 Synthesis of MCM-41 from Different Silica Sources

The method of MCM-41 synthesis was taken place at room temperature under atmospheric condition, following the previous study [10]. Hexadecyltrimethylammonium bromide (CTAB) and two sources of silica; silica extracted from rice husk ash, and commercial sodium silicate, were used as reactants for MCM-41 synthesis; as named RHA_MCM-41 and SDS_MCM-41, respectively. The process of synthesis, called sol-gel method, was carried out with the molar composition of 4SiO_2 : $1\text{Na}_2\text{O}$: 1CTAB : $200\text{H}_2\text{O}$. The mixture was adjusted the pH value to 10 and stirred constantly for 48 h at room temperature. Afterward, the suspended solid was filtered and rinsed with ethanol solution. The filtered solid was calcined at 550 °C for 5 h and kept in the desiccator before characterizations.

2.3 Sample Characterizations

The physical properties and morphology of synthesized samples were examined by various techniques. The study of crystallinity was conducted by an X-ray diffractometer (Miniflex goniometer) using $\text{CuK}\alpha$ radiation in angular range from 1 to 10 °(2θ) with 15 mA and 30 kV.

The surface morphology was studied by SEM (JEOL JSM-6400) operated at 15 kV and TEM (JEOL-JEM-200 CX) operated at 100 kV. The porosity was determined by the nitrogen adsorption data (Autosorb-1, Chrontachrome) and surface area and pore size distribution were calculated on a basis of the BET method and the BJH model.

3. Results and Discussion

3.1 The Extracted Silica Characterizations

The mineral content of the white extract was measured by X-ray Fluorescence Spectroscopy (XRF). The amount of SiO_2 up to 95.62% was obtained by refluxing in 1 M hydrochloric solution. The trace amount of impurities was also found such as Al_2O_3 , K_2O , CaO , MgO , MnO_2 and P_2O_5 .

The XRD pattern of the extracted silica was shown in Fig. 1. A broad peak appeared around 2θ equal to 22° clearly indicated that silica obtained from acid leaching of rice husk ash was in the amorphous form [1-3].

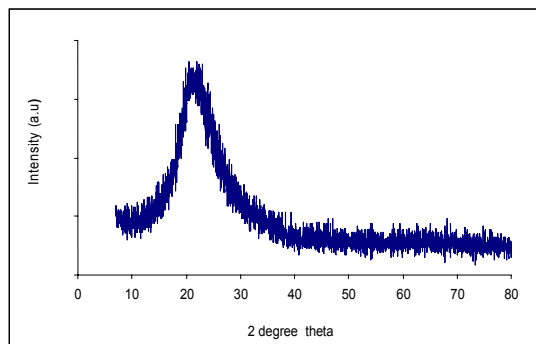


Fig. 1. The XRD pattern of silica extracted from rice husk ash obtained by acid leaching

Structure of Mesoporous MCM-41 Prepared from Rice Husk Ash

The morphology of silica extracted from RHA was shown in Fig. 2 with the magnification of 200 times. Different shapes of silica particles; globular and rectangular shapes, were found in the extract. Even though the grinding of the extract was carried out before SEM measurement, the silica depositing along the skeleton of rice husk (rectangular structure) was remaining in the extract. While the fine silica particles were shown in the globular shapes with the average diameter of 50 μm .

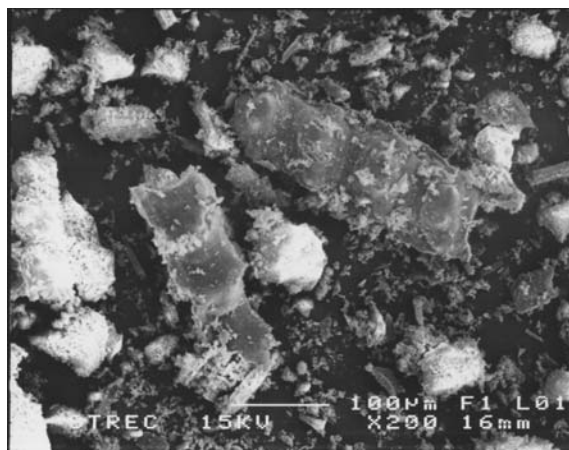


Fig. 2. The SEM image of silica extracted from rice husk ash (x200)

3.2 MCM-41 Characterizations

3.2.1 X-ray Diffraction (XRD)

The crystallinity of MCM-41 synthesized from rice husk ash and sodium silicate was observed by the XRD diffractograms (see Fig. 3). The XRD patterns of RHA_MCM-41 and SDS_MCM-41 were shown in similar manners. Three reflections of silicon dioxide crystals were found at 2θ equal to 2.6° , 4.4° and 5.0° , corresponding to hkl reflection planes 100, 110 and 200, respectively. These sharp signals indicated the long-range orders of the uniform hexagonal mesoporous structure, which is the extraordinarily characteristic of MCM-41 type. According to the results, it was inferred that silica from rice husk ash can be utilized for the synthesis of MCM-41 material instead of using commercial silica.

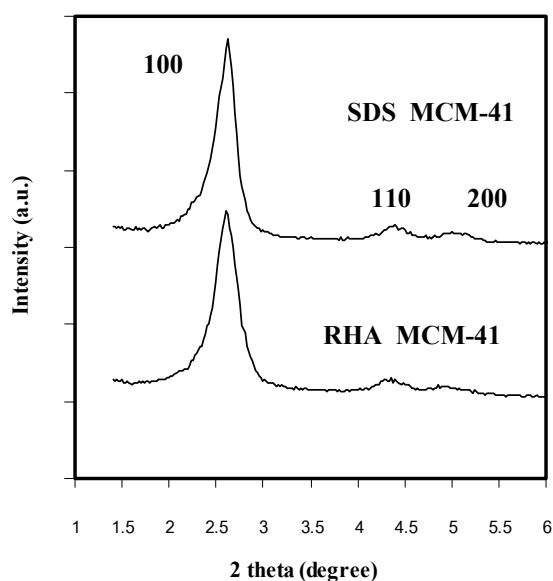


Fig. 3. The XRD patterns of SDS_MCM-41 and RHA-MCM-41

3.2.2 SEM and TEM morphology

During the aging period of 48 h, the silicate species were gradually crystallized in order to form siloxane network (Si-O-Si). The Scanning Micrographs of both MCM-41 (see Fig. 4 and 5) exhibited the agglomerated particles with the uniform size in a range of 0.3-0.5 μm , smaller than that of the extracted silica (50 μm) about 100 order of magnitude. This is because the well-organized assembly of silicate ions reacted with the cationic template in adequate crystallization.

Both top and side views obtained from TEM results indicated the three dimensional images of crystallized MCM-41 (see Fig. 6 and 7). The highly ordered MCM-41 consists of the gathering of rod-like silicates. The cross sectional patterns (top view) showed hexagonal or honey-comb structure which is the distinctive feature of MCM-41. The pore diameters estimated from the top view were approximately 2-3 nm for both MCM-41.

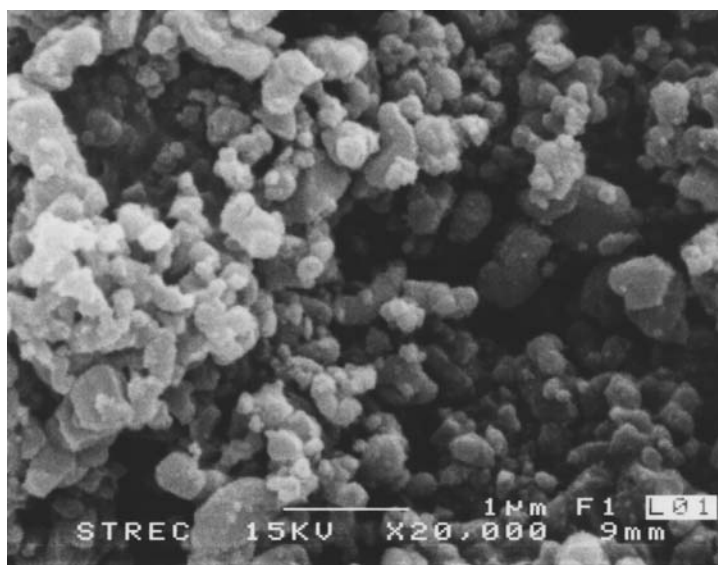


Fig. 4. The SEM images of RHA_MCM-41 (x20,000)



Fig. 5. The SEM images of SDS_MCM-41 (x15,000)

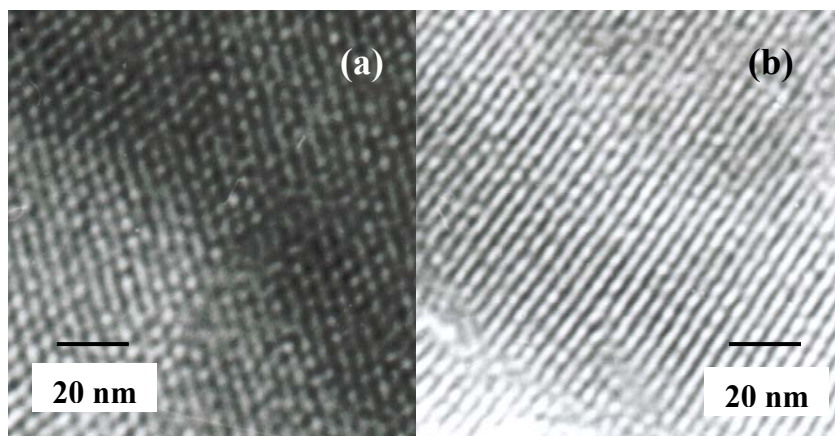


Fig. 6. The TEM images of RHA_MCM-41: top view (a) and side view (b)

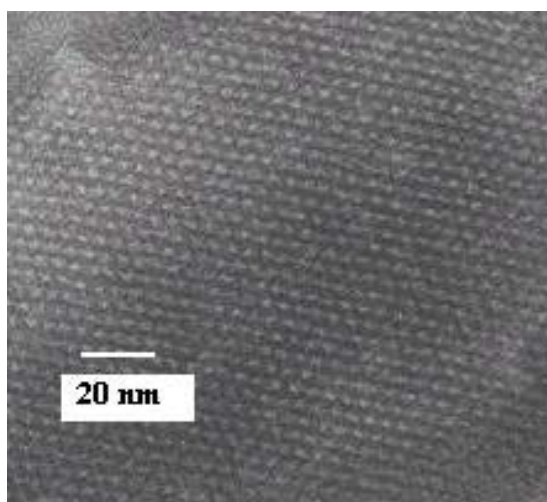


Fig. 7. The TEM images (vertical section) of SDS_MCM-41

3.2.3 Nitrogen Adsorption and Desorption Isotherms

The nitrogen adsorption-desorption isotherms and pore size distributions (PSDs) of the synthesized MCM-41 were shown in Fig. 8 (RHA_MCM-41) and Fig. 9 (SDS_MCM-41). Both plots of isotherms were determined as type IV, according to IUPAC classification. The steep lines and hysteresis loops which occurred at $2.5 < P/P_0 < 3.4$ was the characteristic of mesoporous materials with a narrow range of uniform and cylindrical pores [6-8]. These results were in good agreement with the BJH pore size distribution patterns (see inserted figures). One sharp peak appeared in a range of 1.8-3.0 nm with average pore diameter of 2.2 nm.

The porosity properties obtained from nitrogen isotherms of RHA_MCM-41 and SDS_MCM-41 were tabulated in Table 1. The BET surface area (S_{BET}) of the extracted silica was $153 \text{ m}^2\text{g}^{-1}$, which was much lower than that of the synthesized MCM-41. RHA_MCM-41 possessed the highest surface area of $730 \text{ m}^2\text{g}^{-1}$ while SDS_MCM-41 gave the surface area of $960 \text{ m}^2\text{g}^{-1}$. The average pore diameters calculated by using the BJH model for both synthesized MCM-41 were centered around 2.2 nm. The pore volume of RHA_MCM-41 and SDS_MCM-41 was 0.87 and 0.70 ml g^{-1} , respectively. According to the porosity data, the pore diameter of the MCM-41 particles is not affected by the source of silica but it is significantly controlled by the length of carbon chains in the molecules of organic template.

Table 1. The porosity properties of the extracted silica compared with RHA_MCM-41 and SDS_MCM-41

Samples	Particle size* (μm)	Pore diameter BJH (nm)	Pore volume (ml g^{-1})	S_{BET} ($\text{m}^2 \text{g}^{-1}$)
RHA_Silica**	50	3.6	0.28	153
RHA_MCM-41	0.3	2.2	0.87	730
SDS_MCM-41	0.5	2.2	0.70	960

* The particle sizes estimated from the SEM results
 ** RHA_Silica: the silica extracted from rice husk ash

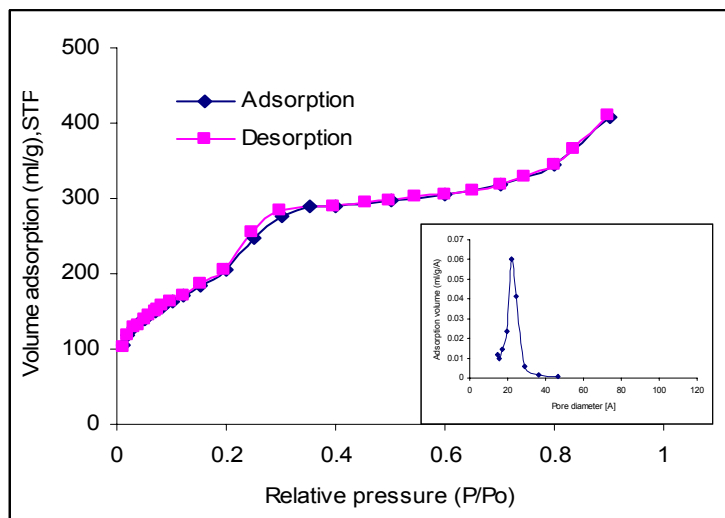


Fig. 8. Nitrogen adsorption and desorption isotherms of RHA_MCM-41 and its pore size distribution

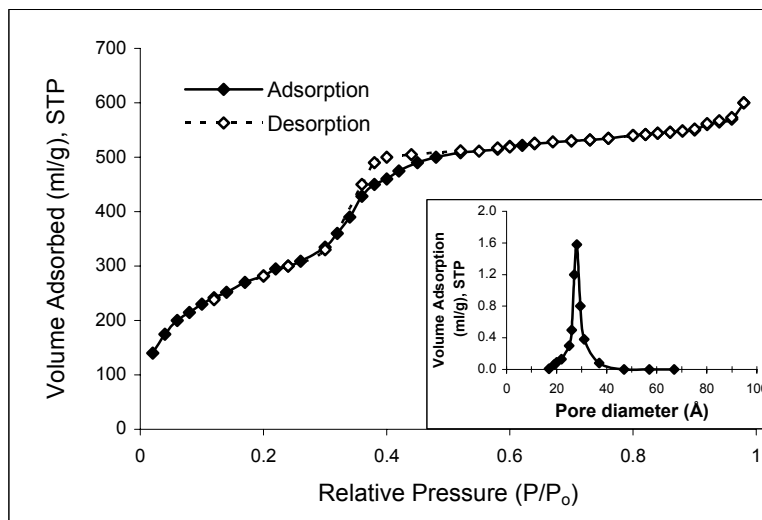


Fig. 9. Nitrogen adsorption and desorption isotherms of SDS_MCM-41 and its pore size distribution

4. Conclusion

Rice husk ash generated from biomass power plant can be utilized for the synthesis of MCM-41. More than 95 % of amorphous silica was obtained from the acid pretreatment of rice husk ash and can be used as a silica source for the synthesis of MCM-41 material. The crystallinity characteristics and the porosity properties of MCM-41 synthesized from rice husk ash were similar to those of MCM-41 synthesized from commercial silica. The nitrogen isotherms of RHA_MCM-41 were type IV with the BET surface area of $730 \text{ m}^2\text{g}^{-1}$. The BJH pore diameter was approximately 2.2 nm and the pore volume was 0.87 ml g^{-1} with a narrow pore size distribution.

References

- [1] Kalapathy U., Protor A. and Shultz J., "A simple method for production of pure silica from rice hull ash", *Bioresource Technology*, Vol. 73, (2000), pp 257-264.
- [2] Riveros H. and Garza C., "Rice husks as a source of high purity silica", *J. Cryst. Growth*, Vol. 75, (1986), pp 126-131.
- [3] Yalcin N., and Sevic V., "Study on silica obtained from rice husk", *Ceramics internationa.*, Vol. 27, (2001), pp 219-224.
- [4] Della V. P., Kuhn I. and Holtza D., "Rice husk ash as an alternate source for active silica production", *Materials Letter.*, Vol. 57, (2002), pp 818-821.
- [5] Krishnarao R. V., Subramanyam T. and Kumar J., "Studies on the formation of black particles in rice husk silica ash", *J. Euro. Cem. Soc.*, Vol. 21, (2001), pp 99-104.
- [6] Beck J. S., Vartuli C., Roth W. J. and Kresge C. T., "Family of mesoporous molecular sieves prepared with liquid crystal templates", *J. Am. Chem. Soc.*, Vol. 114, (1992), pp 10834-10843.
- [7] Zhao S. X., Lu Q. G. and Millar J. G., "Advances in Mesoporous Molecular Sieve MCM-41", *Ind. Eng. Chem. Res.*, Vol. 35, (1996), pp 2075-2090.
- [8] Selvam P., Bhatia K. S. and Sonwane G. C., "Recent Advances in Processing and Characterization of Periodic Mesoporous MCM-41 Silicate Molecular Sieves", *Ind. Eng. Chem. Res.*, Vol. 40, (2001), pp 3237-3262.
- [9] Kumer D., Schumucher K., de Fresne von Hoheneschen C. Grün, M. and Unger K.K., "MCM-41, MCM-48 and related mesoporous adsorbents the synthesis and characterization" *Colloids and Surfaces A: Physicochem. Eng. Aspects.*, Vol.187-188, (2001), pp 109-116.
- [10] Gridanurak N., Chiarakorn S., and Wittayakun J., "Utilization of Mesoporous Molecular Sieve Synthesized from Natural Source Rice Husk silica to Chlorinated Volatile Organic Compounds (CVOCs) Adsorption", *Korean J. Chem. Eng.*, Vol. 20, (2003), pp 950-955.