International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.9, No.08 pp 382-387, 2016

Synthesis of MCM-41-NH_2 Catalyst by Sonochemical Method for Transesterification of Waste Palm Oil

Arini Al Ifah[1], Wega Trisunaryanti[1]*, Triyono[1], and Kumala Dewi[2]

[1]Department of Chemistry, Faculty of mathematics and natural sciences Universitas Gadjah Mada Sekip Utara, Yogya 55281 Faks (0274)545188, Indonesia
[2]Biology, Faculty of Biology Universitas Gadjah Mada Jl. Teknika Selatan, Yogyakarta 55281, Indonesia

Abstract : Synthesis of MCM-41 based on silica from Lapindo mud by sonochemical method grafting with amine group from (3-aminopropyl) trimetoxysilane (3-APTMS) to produce the MCM-41-NH_2 base catalysts had been investigated. The purposes of this research are to study the effect of sonication time towards the crystallinity of the MCM-41 and to verify catalytic activity of the MCM-41-NH_2 catalyst in the transesterification of waste cooking oil. The silica was extracted from Lapindo mud using 6 M of HCl and NaOH solution. The silica content was characterized by XRF. The synthesis of MCM-41 was carried out by sonochemical method under time variation of 30, 60, 90, 120 and 150 min. The Grafting of the 3-APTMS into the MCM-41 was performed in N/Si mol ratio of 5%. The MCM-41 and MCM-41-NH_2 were characterized by XRD, Surface Area Analyzer, and TEM. The GC-MS was used to characterize the transesterification product.
The XRF analysis showed that the silica extracted from Lapindo mud was 97.5 %. The XRD analysis of the MCM-41 for 150 min sonication showed the highest characteristic peaks on 2θ between 2-5^0 with specific surface area of 1603 m^2g^{-1}, pore diameter of 2.57 nm and has a mesoporous character with adsorption and desorption isotherm pattern of type IV and hysteresis loops of type H1. The TEM images of the MCM-41 showed the order pore distribution. The MCM-41-NH_2 catalyst has specific surface area of 1037 m^2g^{-1} with pore diameter of 2.39 nm. Product conversion of transesterification of the waste oil was 76.55 %.
Keywords : Sonochemical, MCM-41, MCM-41-NH_2, Lapindo mud, transesterification.

Introduction

A result of mudflow due to oil and gas exploration activities by PT Lapindo Brantas, Inc. since of Mei 2006 has been soaking approximately 250 ha of land in Sidoarjo, East Java[1,2]. Utilization of Lapindo mud is still limited to create building materials which has low economical value[2]. One method is carried out to produce a high silica content is through the activation of acid and alkaline leaching[3,4]. Sodium silicate of Lapindo mud had been used as a source of silica for synthesis of silica rich material, MCM-41[5-7].

Generally, the MCM-41 is synthesized using hydrotermal method[8,9]. The mixture of reagents of water as a solvent, referring agent structure, and a source of silica in autoclave are heated to a relatively high temperature of 150 ^{0}C for 48 h[9-13]. Tang[14] has synthesized MCM-41 by a sonochemical methods by performing sonication reaction time for 3.5 h. The quality of the MCM-41 was not much different with that of the synthesis of MCM-41 using hydrothermal method**.** The sonochemical method can be used as an alternative method for the synthesis of MCM-41 with a relatively short time. However, the durations of sonication time during the synthesis of MCM-41

are different. It is interesting to come to the idea of conducting a study of sonication time variation to approve the optimum crystallinity of MCM-41.

Transesterification of vegetable oilswas the most important process to provide new and renewable energy sources. The previous works were mainly focus on the transesterification of vegetable oils[15-18]. However, only small portion of them evaluated the transesterification of waste cooking oils[19-21]. Transesterification process can be carried out using acid[15-21]and base catalysts[22-24]. Acid catalysts are not suitable for the environment, on the other hand base catalysts are more eco-friendly. Modification of MCM-41 using (3-aminopropyl) trimetoxysilane (3-APTMS) compound by grafting method was shown a high performance of base catalyst in transesterification of fresh cooking oil to produce biodiesel[5,25].

To utilize the MCM-41 as a catalyst in the waste cooking oil transesterificationprocess the authors undertaken the synthesis of MCM-41 using silica from Lapindo mud, Sidoarjo, by sonochemical method as well as modification of the MCM-41 using (3-aminopropyl) trimetoxysilane (3-APTMS) compound to produce MCM-41-NH_2 as a base catalyst. The catalyst was then utilized in transesterification of waste cooking oil to produce biodiesel.

Experimental

Materials

Lapindo mud produced in Sidoarjo, Indonesia, hydrofluoric acid, methanol,sulfuric acid, *cetiltrimethyl ammonium bromide* (CTAB), Toluene $C_6H_5CH_3$, n-heksene, amine group from (3-aminopropyl) trimetoxysilane (3-APTMS) analytical grade were obtained from E-Merck (Germany).All materials used were analytical grade and used without further purification.

Instrumentation

Ultrasonic Cleaner (Bransonic 220, 48kHz, 100W), sentrifugator (Kokusan H-107), X-ray Diffractometer (XRD, Shimadzu XRD-6000), X-ray Fluoresence(XRF, PANalyticalMiniPal 4), Infrared spectrophotometer (FT-IR,shimadzu Prestige-21), gas chromatography-mass spectrophotometer(GC-MS, Shimadzu QP2010S), *Transmission Electron Microscope* (TEM) JEOL JEM-14000 and gas absorption analysis (GSA, Quantachrome NovaWin2 1200e version2.2).

Procedure

Extraction of silica from Lapindo mud

Lapindo mud was refluxed with 6 M HCl solution at a temperature of 90 ^{0}C for 3 h, then 6 M NaOH solution at 90 ^{0}C for 16 h. The resulting filtrate was separated from the solids by filtration method. The supernatant was titrated using 3 M HCl solution until pH 8. The white precipitate was filtered and washed with distilled water and dried at 100 ^{0}C for 24 h, produce SiO_2 then analized using X-ray Fluoresence (XRF).

Synthesis of MCM-41 by sonochemical method

Silica (SiO_2) was dissolved in 50 mL of distilled water containing 3 g NaOH for 2 h. The 2.187 g CTAB is dissolved in 45 mL of distilled water and added with Na_2SiO_3 solution while stirring until a homogeneous solution was performed. After the reaction was completed, 1 M H_2SO_4 solution was added into the mixture until pH 11 and white gel was performed and continued stirring for 1 h . The gel was sonicated in variation time of 30, 60, 90, 120, and 150 min, then the precipitate was filtered and washed with distilled water until the pH was neutral. The solid was dried in an oven at a temperature of 100 ^{0}C for 5 h. The white solid was then calcined at 540 ^{0}C for 5 h then referred as MCM-41. The MCM-41 was then characterized using X-ray Diffraction (XRD), Transmission Electron Microscope (TEM), and Surface Area Analizer (SAA).

Modification of MCM-41 with 3-APTMS

The 3-APTMS compound was refluxed in toluene solution for about 20 min. at a temperature of 90 ^{0}C. The MCM-41 was calcined and added into the solution. The reflux process was continued for 5 h at a temperature

of 90 ^{0}C. The solid was separated from the solvent by centrifugator in 2000 rpm for 20 min. The solid was then washed with toluene followed by methanol. The solid was then dried at 50 ^{0}C for 24 h produced MCM-41-NH_2. The MCM-41-NH_2 was characterized using XRD, FT-IR, TEM, and SAA.

Transesterification of waste palm oil

The transesterification process was carried out by refluxing a mixture of methanol, waste palm oil and MCM-41-NH_2 as abasecatalyst. The catalyst used was 10 wt.% of the palm oil. After the reflux, the solid was separated using centrifugator at 2000 rpm for 20 min. The products were separated by adding n-hexane to take the organic layer then washed using warm distilled water. The product obtained from the transesterification was then analyzed by Gas Chromatography-Mass Spectrometer (GC-MS) to determine the type of compounds and conversions of the ester.

Result and Discussion

Extraction of silica from the Lapindo mud

The SiO_2 concentration extracted from the Lapindo mud was 97.5 wt.%. This result indicated that the SiO_2 has a high purity to use as a silica resource in the synthesis of the MCM-41.

Synthesis of MCM-41 by sonochemical method

The diffractograms of the synthesized MCM-41 in variation of the sonication time were shown in Fig.1.

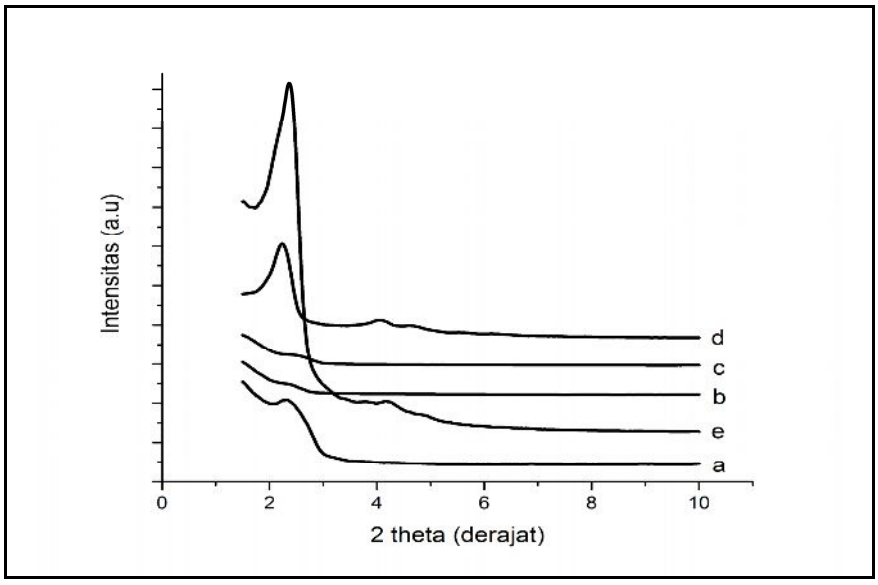

Figure 1. X-ray diffraction pattern of the MCM-41 synthesized under sonication time variations: (a) 30, (b) 60, (c) 90, (d) 120, and (e) 150 min.

The diffractogram showed characteristic sharp peaks at 2θ of about 2.40^0 for the [100] field, which were the characteristic for the hexagonal MCM-41. The result indicated that the increase of sonication time increased the sharpness of the characteristic peaks of the MCM-41, except for the sonication time of 60 and 90 min. The sonication time for 150 min. produce the highest intensity peak of the MCM-41. This may be caused by the energy supply for the formation of the MCM-41 was enough at the time duration of sonication up to 90 min.

Table 1. Results of measurements of specific surface area, pore diameter and total pore volume

Material	Specific surface area (m^2/g)	Average pore diameter (nm)	Pore volume (cc/g)
MCM-41 (150 min.)	1603	5.0	1.0
MCM-41-NH_2	1037	4.8	0.6

Table 1 showed that the MCM-41 has high specific surface area with average pore diameter of 5 nm. This indicated that the MCM-41 has a meso pore size. The surface area and pore diameter were slightly reduced after grafting with the 3-APTMS. The phenomena may be caused by the coverage of a small portion of pores by the 3-APTMS.

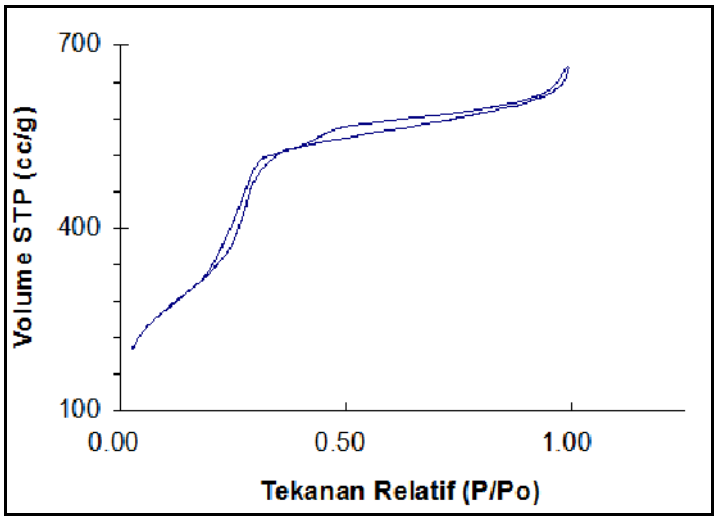

Figure 2. Adsorption-desorption isotherm of N_2 for MCM-41 sonicated for 150 min

Figure 2. Showed the adsorption-desorption isotherms of N_2 for the MCM-41 as type IV isotherm which characteristics of mesoporous materials according to the IUPAC classification. The appearance of hysteresis in the P/P^0 of 0.2 to 0.4 described the monolayer adsorption of nitrogen on the wall of mesoporous.

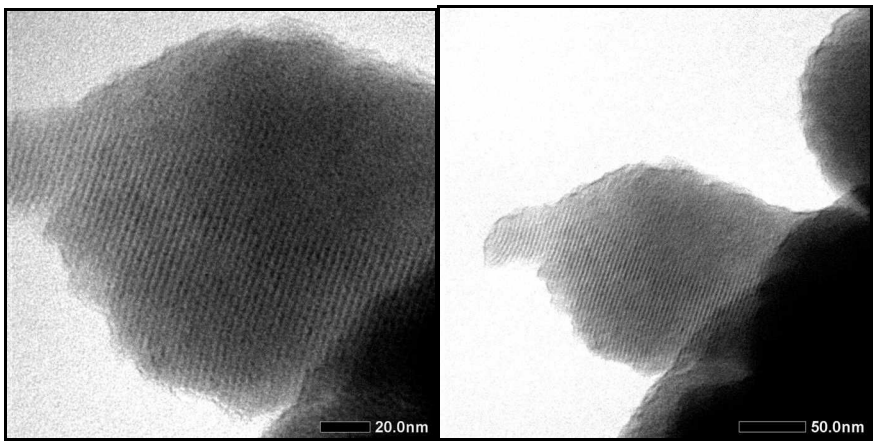

Figure 3. The TEM image of MCM-41 sonicated for 150 min. with the scale of 20 nm and 50 nm

Figure 3 showed that the MCM-41 has a cylindrical pore arrangement, visible black lines that expressed the pore walls, while the white lines are pores arranged in alternating and regular. The TEM image indicated that the MCM-41 has ordered pores shape.

Transesterification of waste palm oil

The transesterification process is intended to test the catalytic activity of the MCM-41-NH_2. The mass spectroscopy showed that the methyl ester produced by the transesterification of waste palm oil was 76.55%.

Conclusion

The MCM-41 sonicated for 150 min. showed the highest performance with ordered mesopore with a pore diameter of 2.5 nm and a specific surface area of 1603 m^2/g. The MCM-41-NH_2 catalyst has a pore diameter of 2.4 nm and a specific surface area of 1037 m^2/g. The transesterification of the waste oil produced methyl ester of 76.55%.

Acknowledgement

This work was financially supported by The Indonesian Ministry of Research, Technology, and Higher Education under research Grand of Penelitian Unggulan Perguruan Tinggi Universitas Gadjah Mada (Contract number: 907/UN1.P.III/LT/DIT-LIT/2016).

References

1. Fadli, A.F., Tjahjanto, R.T., dan Darjito, Ekstraksi Silikadalam Lumpur Lapindo Menggunakan Metode Kontinyu, *Student Journal.,* 2013,1(2), 182-187.
2. Ekaputri, J.J., and Triwulan, Study on Porong Mud Based Geopolymer Concrete, *2nd Asian Concrete Federation Conference,* 2006, 20 – 21 November, Bali.
3. Olawale, Olamide, and Oyawale, F.A., Characterization of Rice Husk via Atomic Absorbtion Spectrophotometer for Optimal Silica Production, *Inter. J. Sci. Tech.*, 2, 2012,210-213.
4. Okoronkwo, E.A., Imosili, P.E., and Olusunle, S.O.O., Extraction and Characterization of Amorphous Silica from Corn Cob Ash by Sol-Gel Method, *J. Chem. Mater. Res*., 2013, 3, 68-72.
5. Triyono, T., Khoiri, H.M., Trisunaryanti, W., and Dewi, K., Synthesis of NH_2/MCM-41 Catalysts using Silica of Sidoarjo Mud and Their Characterization For Palm Oil Transesterification, *IOSR-JAC*., 2015, 8 (8), 50-56.
6. Beck, J.S., Vartuli, J.C., Roth, W.J., Leonowicz, M.E., Kresge, C.T., Schmitt, K.D., Chu, C.T-W., Olson, D.J., Sheppard, E.W., McCullen, S.B., Higgins, J.B., danSchlenker, J.L., 2015, A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates, *J.Am.Chem.Soc*., 2015, 114, 10834-10843.
7. Lisna, P.S., Trisunaryanti, W., Kartini, I., and et al, Extraction of Gelatin from Bovine Bone and its Use as Template in Synthesis of Mesoporous Silica, *A.J.C*., 2016, 28.5, 996-1000.
8. Wu, H.Y., X.L., Yang, C.Y., Chen, X. And Zheng, X.C., Alkali-hydrothermal Synthesis and Characterization of W-MCM-41 Mesoporous Materials with Various Si/W Molar Ratio, *Appl. Surf. Sci*., 2013, 270, 590-595.
9. Kim, Man, J., Jun, S., danRyoo, R., improvement of Hydrothermal Stability of Mesoporous Silica Using Salt : Reinvestigation for Time-Dependece Effects, *J. Phys. Chem. B.,* 1999, 103, 6200-6205.
10. Kresge, C.T., Leonowicz, M.E., Roth, W.J., Vartuli, J.C. And Beck, J.S., Ordered Mesoporous Molecular Sieves Synthesized by Liquid-crystal Template Mechanism, *Nature*, 1992, 359, 710-712.
11. Chakraborty, B. and Viswanathan, B., Surface Acidity of MCM-41 by in-situ IR Studies of Pyridine Adsorption, *Catal. Today,* 1999, 49, 253-260.
12. Suyanta and Kuncaka, A., Utilization of Rice Husk as Raw Material in Synthesis of Mesoporous Silicate MCM-41, *Indo. J. Chem*., 2011, 11(3) 279-284.
13. Tai, X.M., Wang, H.X., and Shi X.Q., A Novel Method for the Synthesis of Mesoporous Molecular Sieve MCM-41, *Chin. Chem. Left*. 2005, 16, 843-845.
14. Tang, X., Liu, S., Wang, Y., Huang, W., Sominski, E., Palchik, O., Koltypin, Y., and Gedanken, A., Rapid Synthesis of High Quality MCM-41 Silica with Ultrasonic Radiation, *J. Chem. Soc., Chem. Commun*., 2000, 2119-2120.
15. Kusuma, R.I., Hadinoto, J.P., Ayucitra, A., Soataredjo, F.E. and Ismadji, S., Natural Zeolite from Pacitan Indonesia, as Catalyst Support for Transesterification of Palm Oil, *Appl. Clay. Clay Sci*., 2013, 74,

121-126.
16. Carmo Jr, A.C., Souza, L.K.C.D., Costa, C.E.F.D., Longo, E. and Zamian, J.R., Production of Biodiesel by Esterification of Palmitic Acid over Mesoporous Aluminosilicate Al-MCM-41, *Fuel*, 2009, 88, 461-468.
17. Ahmed, F., Giwa, S.O, Ibrahim, M., and Giwa, A., Prouction of Biodiesel from Jatropha Curcas Seed Oil Using Base Catalysed Transesterification, *International Journal of ChemTech Research,* 2016, 9(06), 322-332.
18. Aslam, S.S., and Saravanan, C.G, Biodiesel Production from Mahua oil via Catalytic transesterification method, *International Journal of ChemTech Research,* 2015, 8(4), 1706-1709.
19. Rajagopal, K., Johnson. J., and J., Rajadurai, S., Production of Biodiesel from Waste used Cooking Oil using two Different Alkaline Catalysts, *International Journal of ChemTech Research,* 2015, 8(2), 754-759.
20. A. Renita A., and J. Kumar A., Comparison of Homogeneous Base Catalysts and Heterogeneous Base Catalysts for Biodiesel Transesterification of Waste Cooking Oil, *International Journal of ChemTech Research,* 2015, 8(2), 651-654.
21. Shanmugam, M., Abilarasu, A., and Somanathan, T., Catalytic influence of Mo/SBA-15 towards the transesterification reaction using waste cooking palm oil, *International Journal of ChemTech Research,* 2014-2015, 7(2), 499-503.
22. Payawan Jr L.M., Damasco, J.A and Piecco, K.W.E.S., Transesterification of Oil Extract from Locally-Cultivated Jatropha Curcas Using a Heterogeneous Base Catalyst and Determination of Its Properties as a Viable Biodiesel, *Philipp. J. Sci*., 2010, 139(1), 105-116.
23. Venkatesan, C., Cidambaram, M. and Signh A.P., 3-Aminopropyltriethoxysilyl Functionalized Na-Al-MCM-41 Solid Base Catalyst for Selective Preparation of 2-Phenylpropionitrile from Phenylacetonitrile, *Appl. Catal. A-Gen*., 2005, 292, 344-353.
24. Cao, J., Wu, Y., Jin, Y., Zilihan, P. and Huang, W., Response Surface Methodology Appoarch for Optimization of the Removal of Chromium (VI) by NH_2-MCM-41, *J. Taiwan Inst. Chem. Eng*., 2014, 45, 860-868.
25. Iliade, P., Miletto, Shadjou, N., Chen, S.T. and Sheikhzadeh, P., Funcionalization of Mesoporous MCM-41 with Aminopropyl Groups by Co-condensation and Grafting: A Physico-chemical Characterization, *Res. Chem. Intermed*., 2012, 38, 785-794.

*****