CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 10, No. 1, 2016 Chemical Technology

Hartati Hartati, Alfa Widati, Harsasi Setyawati and Sarita Fitri

PREPARATION OF HIERARCHICAL ZSM-5 FROM INDONESIAN KAOLIN BY ADDING SILICA

Department of Chemistry, Faculty of Science and Technology,
Universitas Airlangga, Surabaya 60115, Indonesia; hartatidodit@yahoo.com

Received: March 23, 2015 / Revised: April 01, 2015 / Accepted: May 23, 2015

Abstract. Hierarchical ZSM-5 was prepared using Bangka kaolin-Indonesia in the absence of structure directing agent. The effect of hydrothermal time and temperature was investigated. The prepared samples were characterized by XRD, XRF, FT-IR, and N_2 adsorption/desorption. The results show that hierarchical ZSM-5 can be obtained at hydrothermal temperature of 393–448 K. Moreover, this method also produces mordenite and quartz as by-products.

Keywords: hierarchical ZSM-5, Bangka kaolin-Indonesia, hydrothermal time and temperature.

1. Introduction

Development of porous material with a higher surface is widely investigated such as adsorption, chromatography, catalysis, sensor, and gas storage [1-4]. Hierarchical is one of the pore modification technologies. Hierarchical ZSM-5 is synthesized and used in the selective condensation of benzaldehyde with 2-hydroxy-acetophenone, esterification of benzaldehyde with hexanoic acid, as well as branched polyethylene [5]. Moreover, hierarchical ZSM-5 shows better catalytic activity to convert methanol than using conventional ZSM-5 as a catalyst [6].

A bulk of works has been reported on preparation of hierarchical ZSM-5. Some researchers reported preparation of hierarchical ZSM-5 by post synthesis as demetalisation and desilication without organic template done [7-9], while the other researchers published the synthesis of hierarchical ZSM-5 by direct template (supramolecular and solids template) [10-13]. The synthesis also requires silica and alumina source, in order to decrease the cost of ZSM-5, many researcher substituted the commercial chemical products by the natural ones. Rice husk ash, fly ash, and kaolin are some materials that have been used for synthesis of zeolite as a source of silica and/or alumina [14-16].

In Indonesia kaolin is a clay mineral reserved in large abundance which reaches 1,068,377,264 tons. Bangka Belitung is the largest mine of kaolin in Indonesia [17]. Generally, kaolin contains 10–95 % of minerals and 85–95 % of kaolinite ($2H_2O\cdot Al_2O_3\cdot 2SiO_2$) [18]. Kaolin may also contain quartz, mica, feldspar, illite, montmorillonite, and a bit of bauxite, zircon, rutile, kyanite, siliminate, graphite, attapulgite and halloysite [19]. The kaolin is used for the synthesis of ZSM-5, for example for the synthesis of ZSM-5 micropores. However, kaolin structure is constructed of a silicon tetrahedral layer and a layer of silicon octahedral units (1:1 clay mineral), causing difficulties to synthesize zeolite directly from kaolin [20]. Therefore kaolin must be enabled to change its structure by metakaolinization. Metakaolin was observed through calcination of kaolin at the temperature of 873–1173 K [21]. In this paper we present a synthesis method to prepare hierarchical ZSM-5 from metakaolin without the addition of structure directing agent. The effect of hydrothermal time and temperature in the synthesis process was examined. The products were characterized by XRD, XRF, FT-IR, and N_2 adsorption/desorption.

2. Experimental

2.1. Material Preparation

ZSM-5 was prepared by using Bangka Belitung kaolin as a raw material, tetraethylorthosilicates (TEOS) as an additional silicon source, sodium hydroxide (NaOH) as a mineralizing agent and provides alkalinity, cethyltrimethylammonium romide (CTAB) as a mesophase template, and silicalite-1 as a seed. All reagents were purchased from Merck, analytical grade and used as received without further purification.

Firstly, the activation of kaolin to metakaolin was observed by a calcinations process under 923 K for 8 h. After that, metakaolin and TEOS were mixed under stirring for 12 h at room temperature. The molar composition of the solution is $10Na_2O:100SiO_2:2Al_2O_3:1800H_2O$. Next, the gel was transferred into a stainless steel autoclave at 353, 393 and 448 K for 11, 24 and 48 h. In order to create the mesophase, CTAB with molar ratio of SiO_2/CTAB = 3.85 was slowly added to the precursor solution under stirring at room temperature. This final mixture was aged for 3 h at room temperature. The resulting solid was collected by filtration, and calcinations under N_2 condition for 1 h followed by air calcinations for 6 h.

2.2. Characterization

The X-ray diffraction (XRD) analysis was performed on JEOL JDX-3530 using Cu Kα radiation of 0.15418 nm wavelength. Diffraction data were recorded between 5–50º. Fourier Transform Infra Red (FTIR) spectrum was recorded on the Shimadzu FTIR 8400S.

3. Results and Discussion

3.1. Synthesis of Hierarchical ZSM-5

The transformation of kaolin into metakaolin is the change of crystalline structure into amorphous one. The amorphous structure is more possible to be a raw material in the synthesis process. Characterization of metakaolin was performed using XRD. The results of the XRD analysis show that kaolin has a peak at 2θ 8.86; 12.31; 24.88 and 26.61° (Fig. 1a). Peak at 8.86° is the peak of associated minerals contained in the kaolin Bangka. Peak at 12.31 and 24.88° is the typical peak of kaolin. Meanwhile, peak at an angle of 26.61 ° is the typical peak of quartz [22]. The difference of calcined (metakaolin) and uncalcined kaolin is determined by the peak at 2θ of 12.31° as the characteristic peak of kaolin (Fig. 1b). The loss of this peak at calcined kaolin can be evidence that the sample of kaolin has been transformed into metakaolin. Based on XRF results, metakaolin has 54.3 % SiO_2 and 38.6 % Al_2O_3.

Hierarchical ZSM-5 is synthesized by using metakaolin through variation of hydrothermal time (11, 24, and 48 h) and temperature (353, 393 and 448 K). Hierarchical ZSM-5 was synthesized using a molar ratio composition $10Na_2O:100SiO_2:2Al_2O_3:1800H_2O$ with the addition of CTAB with a molar ratio SiO_2/CTAB = 3.85. As ZSM-5 is a zeolite with large Si/Al ratio, it is necessary to add tetraethyl orthosilicate (TEOS) as a source of additional silica in metakaolin. The mixture of metakaolin, TEOS and NaOH is aged for 12 h. The next process is the hydrothermal process when the amorphous gel is converted into a more crystalline phase. The reaction that occurs during the hydrothermal process is a condensation reaction, which allows the termination and reestablishment of Si, Al–O–Si, Al [24]. Surfactant was added to the mixture with molar ratio SiO_2/CTAB = 3.85 to form hexagonal surfactant system. Prepared sample was calcined to remove organic material within the channel pore of the sample; therefore the active site can be accessed by a reactant molecule in a catalysis application.

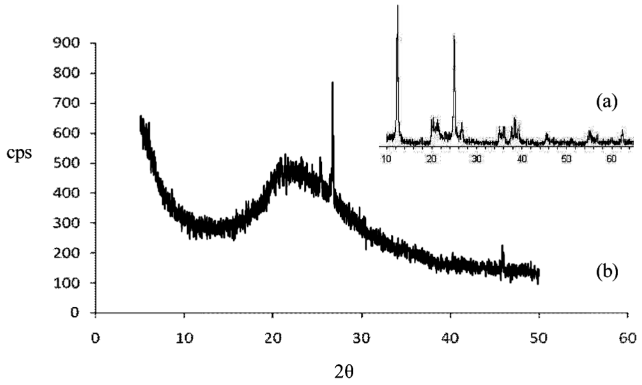

Fig. 1. XRD analysis of uncalcined (a) kaolin (Ref.[23]) and calcined kaolin (metakaolin) (b)

3.2. Sample Characterization

The characteristic of XRD diffractogram peaks of ZSM-5 is 2θ 7.9, 8.9, 23.2, 23.7, 24.1 and 24.9º. XRD pattern shown in Fig. 2 indicates that samples at hydrothermal temperature of 353 K consist of amorphous material; the typical peak of ZSM-5 appears to be of low intensity. At the hydrothermal temperature of 393 K for 11 h transformation of amorphous aluminosilicate into ZSM-5 crystalline was observed. The higher hydrothermal time, the higher intensity peak of ZSM-5. A sharp and high intensity of diffraction pattern can be observed in the samples at the hydrothermal temperature of 448 K, indicating high cystallinities compared with others. It is a peak at 25.6° in the samples at hydrothermal temperature of 393 K and a peak at 26.5° in the samples at hydrothermal temperature of 448 K. Diffraction peaks at 25.6 and 26.5° correspond to mordenite and quartz material, respectively.

The hierarchical structure of the synthesized samples was verified by N_2 adsorption/desorption. Table 1 shows the data of micropore and mesopore areas. The results show that samples with hydrothermal temperature of 393 K expose the presence of micropore and mesopore areas, which represent the hierarchical ZSM-5. These data are not observed in the samples with hydrothermal temperature of 448 K due to the small surface area. Meanwhile, the samples at hydrothermal temperature of 353 K also reveal the hierarchical material but it is not hierarchical ZSM-5.

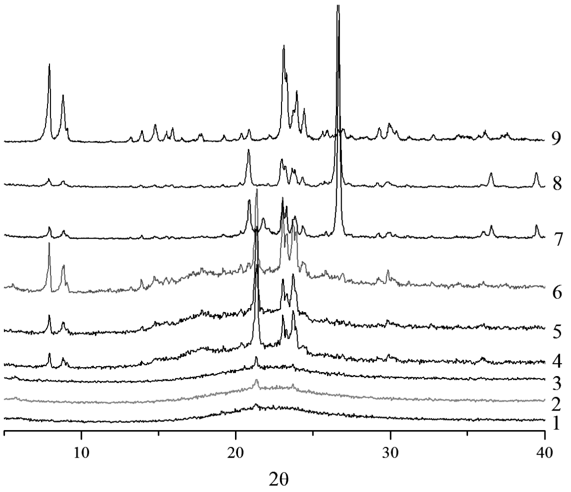

Fig. 2. Samples diffractogram at different hydrothermal temperature and time: 353 K, 11 h (1); 353 K, 24 h (2); 353 K, 48 h (3); 393 K, 11 h (4); 393 K, 24 h (5); 393 K, 48 h (6); 448 K, 24 h (7) and 448 K, 48 h (8). Reference sample of ZSM-5 (9) is given for the comparison

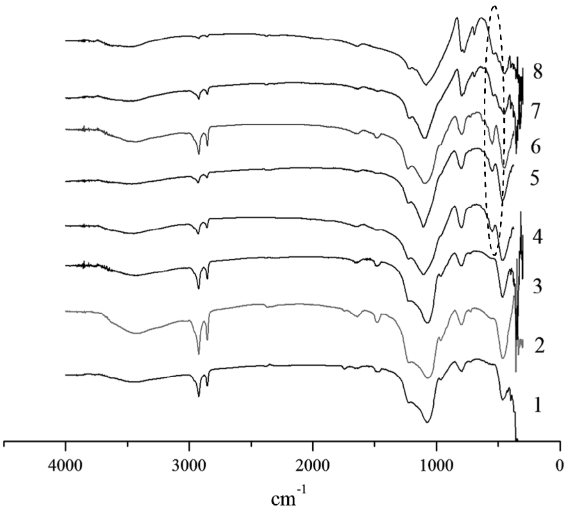

Fig. 3. FT-IR spectra of samples at different hydrothermal temperature and time: 353 K, 11 h (1); 353 K, 24 h (2); 353 K, 48 h (3); 393 K, 11 h (4); 393 K, 24 h (5); 393 K, 48 h (6); 448 K, 24 h (7) and 448 K, 48 h (8)

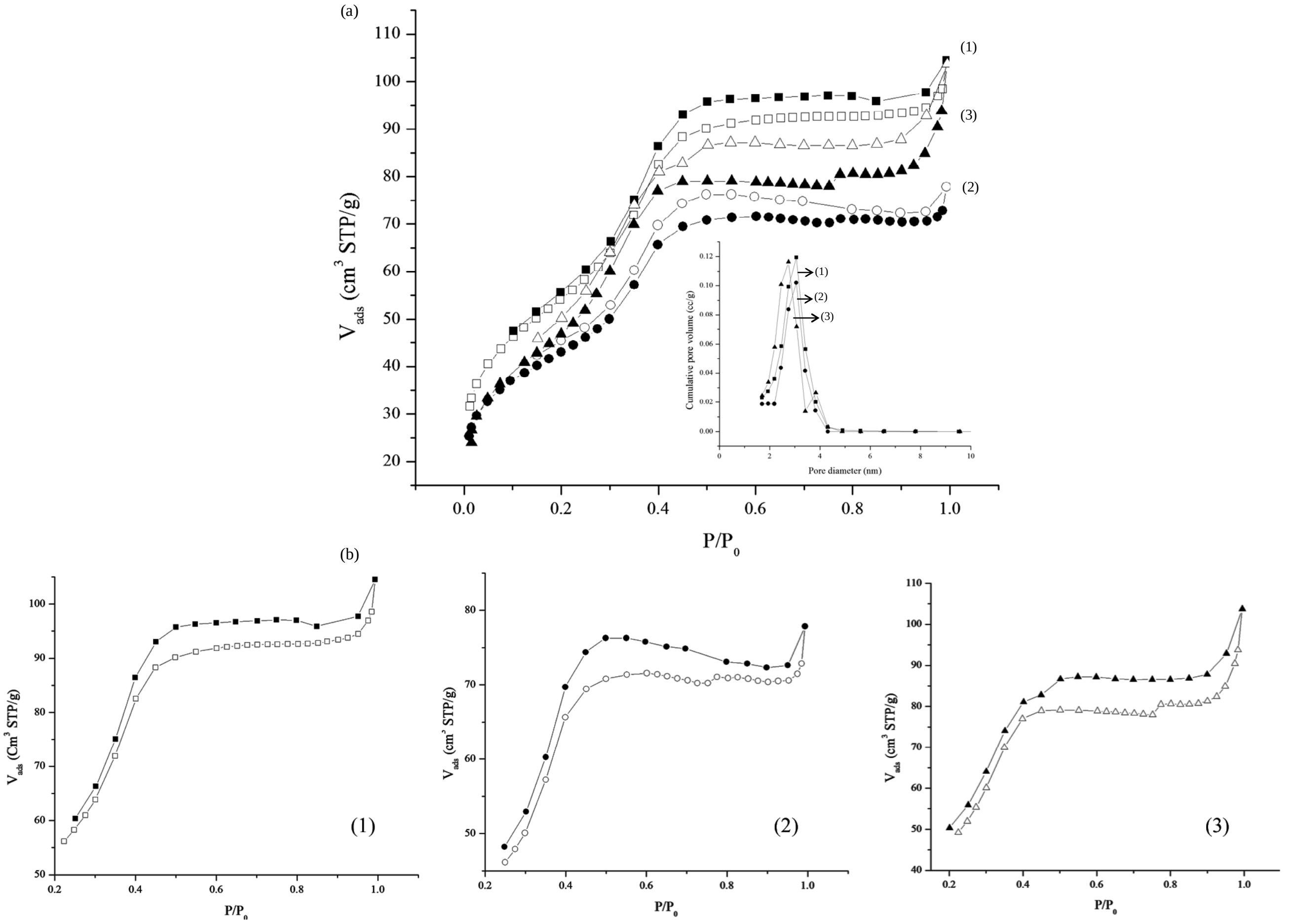

Fig. 4. N_2 adsorption/desorption isotherms (a) and hysteresis loop (b) of the samples at different hydrothermal temperature and time: 393 K, 11 h (1); 393 K, 24 h (2) and 393 K, 48 h (3)

Table 1

Micropore and mesopore areas of samples

Sample	Micropore area, m^2/g	Mesopore area, m^2/g
353 K, 24 h	361.033	441.509
393 K, 11 h	197.437	203.215
393 K, 24 h	154.472	154.387
393 K, 48 h	185.249	208.523
448 K, 24 h	68.375	81.661

Fig. 4a displays the N_2 adsorption/desorption isotherms of samples with hydrothermal temperature of 393 K. All curves indicate the existence of mesopore with 2–3 nm pore diameter. The N_2 isotherms are of type IV accompanied by the type H4 (Fig. 4b). H4 hysteresis loops are generally observed with materials containing both micropores and mesopores [27] that clearly confirms the presence of hierarchical structure located in samples with hydrothermal temperature of 393 K.

4. Conclusions

ZSM-5 was successfully synthesized using Bangka Belitung kaolin without structure directing agent. The crystallinity of the sample increases with increasing hydrothermal temperature and time. Among all synthesized samples the sample at hydrothermal temperature of 393 K is found to be the hierarchical one. However, this method also produces mordenite and quartz as by-products.

References

[1] Perez-Ramırez J., Christensen C., Egeblad K. *et al.*: Chem. Soc. Rev., 2008, **37**, 2530.

[2] Yang J., Yu S., Hu H. *et al.*: Chem. Eng. J., 2011, **166**, 1083.

[3] Su B., Sanchez C., Yang X. *et al.*: Hirarkisly Structured Porous Materials: from Nanoscience to Catalysis, Wiley, Weinheim 2012.

[4] Na K., Choi M., Ryoo R. *et al.*.: Micro. Meso. Mat., 2013, **166**, 3.

[5] Shetti V., Kim J., Srivastava R. *et al.*: J. Catal., 2008, **254**, 296.

[6] Schmidt F., Lohe M. and Büchner B.: Micro. Meso. Mat., 2013, **165**, 148.

[7] Groen J., Bach T., Ziese U. *et al.*: J. Am. Chem. Soc., 2006, **127**, 10792.

[8] Perez-Ramírez J., Verboekend D., Bonilla A. *et al.*: Adv. Funct. Mater., 2009, **19**, 3972.

[9] Kim S., Noh H., Park J. *et al.*: Micro. Meso. Mat., 2006, **92**, 181.

[10] Xiao Q., Yao Q., Zhuang J. *et al.*: J. Colloid Interf. Sci., 2013, **394**, 604.

[11] Egeblad K., Christensen C., Kustiva M. *et al.*: Chem. Mater., 2008, **20**, 946.

[12] Tao Y., Kanoh H., Abrams L. *et al.*: Chem. Rev., 2008, **108**, 896.

[13] Vempati R., Borade R., Hegde R. *et al.*: Micro. Meso. Mat., **93**, 134.

[14] Wang X., Xu H., Fu X. *et al.*: J. Mol. Catal. A, 2005, **238**, 185.

[15] Prasetyoko D., Ayunanda N., Fansuri H. *et al.*: ITB J. Sci., 2012, **44A**, 250.

[16] Murray H.: Applied Clay Mineralogy. Elsevier, Netherland 2007.

[17] Grim R.: Clay Mineralogy. Mcgraw-Hill, New York 1968.

[18] Adamis Z.: Bentonite, Kaolin and Selected Clay Minerals. World Health Organization, Geneva 2005.

[19] Liu B., Li C., Ren Y. *et al.*: Chem. Eng. J., 2012, **210**, 96.

[20] Solcimani M., Naghizadch R., Mirhabibi A. *et al.*: Iranian J. Mat. Sci. Eng., 2012, **9**, 43.

[21] Rios C., Willimas C. and Fullen M.: Appl. Clay Sci., 2009, **42**, 446.

[22] Wibowo W., Ariyanto A. and Sekarini S.: Middle East J. Sci. Res., 2010, **5**, 435.

[23] Cundy C. and Cox P.: Chem. Rev., 2003, **103**, 663.

[24] Flanigen E.: Structural Analysis by Infrared Spectroscopy [in:] Rabo J. (Ed.), Zeolite Chemistry and Catalysis. ACS, Washington 1976.

[25] Zhang A., Li Z. *et al.*: Appl. Surf. Sci., 2008, **254**, 6298.

[26] Thommes M.: Chemie Ingennieur Technik, 1010, **82**, 1059.

[27] Sing K., Everett D., Haul R. *et al.*: Pure Appl. Chem., 1985, **57**, 603.

ПРИГОТУВАННЯ ІЄРАРХІЧНОГО ЦВМ-5 З ІНДОНЕЗІЙСЬКОГО КАОЛІНУ ДОДАВАННЯМ ДІОКСИДУ КРЕМНІЮ

Анотація. *З використанням каоліну Bangka (Індонезія) за відсутності структуроутворюючого агента приготовано ієрархічний ЦВМ-5. Досліджено вплив температури і тривалості гідротермального процесу. Приготовлені зразки охарактеризовано за допомогою рентгеноструктурного, рентгенофлуоресцентного аналізу, Фур'є-спектроскопії та N_2-адсорбції/десорбції. Показано, що ієрархічний ЦВМ-5 можна отримати за гідротермальної температури 393–448 К. Встановлено, що морденіт і кварц отримано як побічні продукти.*

Ключові слова: *ієрархічний ЦВМ-5, Індонезійський Bangka каолін, гідротермальний час й температура.*