Asian Journal of Chemistry; Vol. 28, No. 1 (2016), 211-215

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.19348

Synthesis of ZSM-5 Directly from Kaolin without Organic Template: Part-1: Effect of Crystallization Time

D. HARTANTO[1], O. SAPUTRO[1], W.P. UTOMO[1], A. ROSYIDAH[1], D. SUGIARSO[1], T. ERSAM[1], H. NUR[2] and D. PRASETYOKO[1,*]

[1]Department of Chemistry, Institut Teknologi Sepuluh Nopember, Surabaya, Indonesia
[2]Ibnu Sina Institute for Scientific and Industrial Research, Universiti Teknologi Malaysia, Johor, Malaysia

*Corresponding author: Fax: +62 31 5928314; Tel: +62 31 5943353; E-mail: didikp@chem.its.ac.id

Received: 15 May 2015; *Accepted*: 13 July 2015; *Published online*: 5 October 2015; AJC-17577

Zeolite socony mobile-5 (ZSM-5) have been successfully synthesized directly from kaolin without using organic templates. ZSM-5 were synthesized by hydrothermal method at 175 °C with variation on crystallization time of 12, 24, 48 and 72 h. The molar composition of the zeolites was $10Na_2O:100SiO_2:Al_2O_3:1800H_2O$. The analysis of both from X-ray diffraction and FT-IR spectra showed that the ZSM-5 started to be formed during the crystallization time of 12 h. ZSM-5 with crystallization time of 24 h exhibit the highest crystallinity, about 101.17 % based on the reference. The crystallinity decrease on the crystallization time of 48 and 72 h. In addition, the surface morphology of ZSM-5 investigated by SEM showed that the sample with Si/Al ratio of 5.74-9.49 with variation time of 24, 48 and 72 h formed aggregate with a hexagonal crystal shape without sharp angle. However, the samples with crystallization time of 12 h showed irregular shape.

Keywords: Kaolin, Kaolinite, ZSM-5, Zeolite, Hydrothermal, Synthesis.

INTRODUCTION

Indonesia is rich of kaolin mineral. Based on Central Data of Ministry of Energy and Natural Resources (ESDM) [1], kaolin reserves in Indonesia reaches 1,036,857,260 tons in 2010 [1]. Basically, kaolin is mineral containing kaolinite, dickit, nakrit and halloysite mineral [2]. This material is commonly used in industrial paints, plastics, rubber, cement and paper [3]. In addition, the product of calcined kaolin, metakaolin, is widely used as a base material for zeolite synthesis [4].

Zeolites are crystalline aluminosilicate that synthesized using metakaolin as a source of silica and alumina. Zeolite 4A and analcime have been synthesized from metakaolin using calcination process [5-7]. In addition, mordenite could be synthesized from kaolin before calcination process [8].

Zeolite socony mobile-5 (ZSM-5) has also been synthesized from metakaolin [9,10]. The use of silica and alumina sources of natural materials such as kaolin, fly ash and rice husk ash can reduce the cost of base material for synthesis process.

Synthesis of ZSM-5 is often carried out by hydrothermal method with silica, alumina and metal cation as precusor in presence of organic templates. However, the use of tetrapropylammonium cation (TPA^+) as the most effective organic template in the synthesis of ZSM-5 has lead to a lot of problems, such as cost cosuming, toxicity and difficulty to be degraded. In addition, the release of the organic template in the structure of ZSM-5 during calcination resulted in cracking and decreasing in the crystal lattice in ZSM-5 structure [11,12]. Therefore, research on the synthesis of ZSM-5 without organic template is started to be developed. Kim *et al.* [12] synthesized ZSM-5 without organic template through two stages. The stages consist of nucleation stage at 190 °C and crystallization stage at 150-165 °C. Many researches on the field of zeolites synthesis without organic templates use seed to help crystal formation and to reduce crystal impurities during synthesize process [13].

In this work, ZSM-5 were directly synthesized from kaolin without organic template with the addition of silicalite seed. The crystallization time was varied with variation of 12, 24, 48 and 72 h. The effect of the crystallization time are discussed.

EXPERIMENTAL

All materials used in this work were analytical grade. Sodium hydroxide (99 %) and tetraethylsilicate (TEOS, 98 %) were purchased from Merck, Germany. LUDOX (30 % Si in water) was purchased from Aldrich, Germany. Kaolin (containing 57 % SiO_2 and 22 % Al_2O_3) was taken from from Bangka Belitung, Indonesia. The self-synthesized silicalite was used as the seed.

Synthesis of ZSM-5: ZSM-5 were synthesized directly from kaolin without organic template. The crystallization times varied with variation of 12, 24, 48 and 72 h. The synthesis method was adopted from the method reported by Prasetyoko *et al.* [14]. The molar ratio composition of zeolites was $10Na_2O:100SiO_2:2Al_2O_3:1800H_2O$. Synthesis was started by weighing the demineralized water and dividing it into two parts. In the first half of demineralized water, 1 g of NaOH was dissolved. Then 1.15 g of kaolin was added under stirring. 22.83 g of LUDOX was then added and the stirring speed was increased. After the addition of silica sol (LUDOX), a homogeneous solution was formed. Meanwhile, the second half demineralized water was then added to the solution. The mixture was stirred at 550 rpm for 8 h. After stirring, the mixture was left for 12 h at room temperature. 0.09 g of silicalite was added as the seed of ZSM-5. After addition of silicalite, the hydrothermal process was carried out at 175 °C with variation time of 12, 24, 48 and 72 h, denoted as ZSM-5/12, ZSM-5/24, ZSM-5/48 and ZSM-5/72. The formed solid was washed with distilled water and dried in an oven at 110 °C for 12 h.

The crystal phase of the syntesized zeolite was identified using X-ray diffraction (XRD) with CuK_α (λ = 1.5405 Å) radiation in 2θ from 5-40° with scanning step of 0.04°/sec. The crystallinity of synthesized zeolites were calculated using eqn. 1 using reflection at 2θ = 22.5-25°. Silicalite diffraction patterns is used as the reference reflection. The functional group contained in the zeolites was examined using FT-IR at wavenumber range from 4000-400 cm^{-1}. The zeolites morphologies were investigated using scanning electron microscope equipped with enegy dispersive X-ray (SEM-EDX) to confirm the Si/Al ratio.

$$\text{Crystallinity (\%)} = \frac{\text{Sample reflection intensity}}{\text{Reference intensity}} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

Synthesis of zeolite socony mobile-5 (ZSM-5): Synthesis was carried out with the molar composition of $10Na_2O:100SiO_2:2Al_2O_3:1800H_2O$. Silicalite seed was added in amount of 1 % of the mass of solids. Precursors including kaolin were used as a source of alumina and silica. Silica sol (LUDOX) is used as an additional source of silica, NaOH as a source of Na^+ ions and as mineralization agent. The presence of NaOH has function to trigger the crystal formation. Silicalite seed crystals with MFI structure was added to help initiating the formation of ZSM-5 crystal and demineralized water was added as a source of H_2O. The synthesis stages includes hydrolysis, gelation, aging and crystallization.

Synthesis was begun by dissolving NaOH in demineralized water. Then, the kaolin was added under stirring using magnetic stirrer. Silica sol (LUDOX) was added slowly to the mixture. The stirring was continued at the speed of 550 rpm for 8 h at room temperature to homogenize the mixture. In homogenous mixture, the composition of every part of the mixture were dispersed. In this process, hydrolysis and gelation stages occurred and produced a thick white gel. Furthermore, the aging process was carried out for 12 h. This aging process lead to the formation of bond and structural rearrangement of the solid and liquid phase [15]. After aging, the silicalite seed was added and stirred to disperse it. Once completed, the hydrothermal process was carried out at 175 °C with variation on crystallization time of 12, 24, 48 and 72 h. In general, reaction occured in the synthesis is:

$$Al_4Si_4O_{10}(OH)_8(s) + H_2O(l) + NaOH(aq) + SiO_3(aq) \rightarrow Na_n[Al_nSi_{96-n}O_{192}]\cdot 16H_2O\ Si(OH)_4(aq) \quad (2)$$

Reactions in eqn. 1 occurs at high temperatures in a closed environment with water solvent. The system was closed so the composition of the reactants will not be changed or reduced. In the hydrothermal process, the condensation reaction allows for the formation of new bonds between atoms such as Si, Al-O-Si, Al (TOT) [13]. The resulted solid was washed using distilled water until it reaches neutral pH and then dried in an oven at 110 ºC for 12 h to remove residual water from washing process.

Characterization of ZSM-5

X-ray diffraction (XRD): X-ray diffraction pattern of kaolin, silicalite and ZSM-5 with crystallization time of 12, 24, 48 and 72 h are shown in Fig. 1. The characteristic reflections of kaoline is identified by the presence of reflections at 2θ of 12.32; 19.87; 20.34; 24.85; 26.61; 28.51; 34.95; 35.40; 35.91; 38.37 and 39.22° (Fig. 1a). The XRD pattern of kaolin has a sharp reflections at 2θ of 12.3 and 24.8° and small broad reflections at 2θ 20.5 and 35-38.5°. These results are similar with previous report by Alkan *et al.* [16].

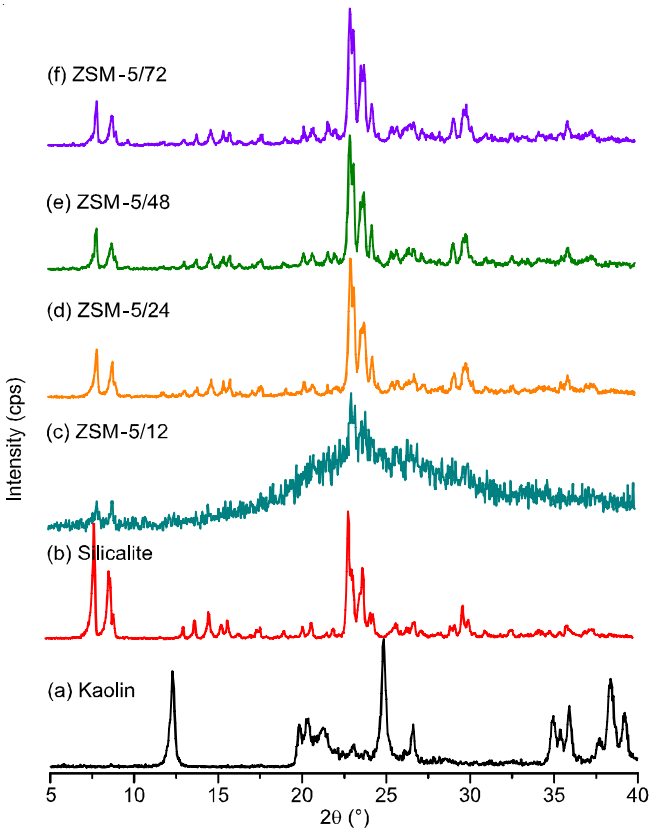

Fig. 1. XRD patterns of the samples (a) kaolin, (b) silicalite and ZSM-5 with a time of crystallization (c) 12, (d) 24 (e) 48 and (f) 72 h

The amorphous ZSM-5 is appeared on the crystallization time of 12 h by the presence of hump at 2θ 17-33°. Comparing

to the kaolin pattern which exhibits high intensity reflections, the hump indicates that the kaolin as zeolite precursor forms amorphous silica phase after hydrothermal process for 12 h. However, the presence of characteristic reflections of ZSM-5 with low intensity in ZSM-5/12 sample at 2θ 7.9, 8.7 and 23.13° indicates that the ZSM-5 crystal has begun to be formed. This result suggest that ZSM-5 with crystallization time of 12 h is still in the early stages of crystal nucleation process.

The characterisic reflections of ZSM-5 are appeared on ZSM-5/24, ZSM-5/48 and ZSM-5/72 samples as shown in Fig. 1d-f. These reflections appear at 2θ 7.85, 8.78, 22.99, 23:21, 23.61, 23.81 and 24.29°. Based on the these XRD patterns, the patterns seem to have the same characteristic reflections. This suggests that all three samples have the same phase. Analysis of the sample's reflections based on XRD powder patterns for zeolites indicates that the pattern of reflections with 2θ of 7.94, 8.8, 8.9, 23.1 and 23.98° is in good accordance with the MFI (inverted mordenite framework) zeolite structure type, therefore, ZSM-5 samples with crystallization time of 24, 48 and 72 h of have MFI structure [17].

In addition to the pattern reflections at the same 2θ, XRD patterns of ZSM-5/24, ZSM-5/48 and ZSM-5/72 exhibit sharp reflections with high intensity. This result indicates that all of these samples are crystalline solids. Therefore, to determine the degree of crystallinity, the crystallinity was calculated using eqn. 1. The results of calculations are presented in Table-1.

TABLE-1
CRYSTALLINITY IN ZSM-5 WITH A VARIATION OF CRYSTALLIZATION TIME

2θ (°)	Intensity (cps)			
	ZSM-5/12	ZSM-5/12	ZSM-5/12	ZSM-5/12
7.85-7.89	18.48	203.23	163.99	169.54
8.78-8.81	19.91	137.09	112.35	107.95
22.99-23.03	45.51	588.37	573.54	538.98
23.21-23.24	-	462.41	446.6	413.87
23.61-23.67	-	283.4	269.21	296.61
23.81-23.87	-	308.74	298.13	258.52
24.29-24.32	-	162.89	176.24	151.94
Crystallinity (%) (average)	2.55	101.17	98.81	93.00

ZSM-5/24 samples exhibits the highest crystallinity. It is about 101.17 % relative to the reference. However, the crystallinity of the sample does not increase with the increasing of crystallization time (48 and 72 h). Prasetyoko and Ayunanda [14] reported that the solution of amorphous silica systems tends to form stable crystals at high temperature. Thus we predict that the formed ZSM-5 crystals were dissolved again to the solution forming more stable crystal within crystallization time of 48 and 72 h. In this study, the crystallization time was very influential on the formation of ZSM-5 crystals in which the optimum formation time of ZSM-5 is for 24 h at a temperature of 175 °C and the crystallinity of the solids is 101.17 %.

Infrared spectroscopy: Analysis of infrared spectroscopy is used to determine functional group in synthesized solid. Kaolin sample exhibits bands at wavenumbers 429, 468, 540, 697, 757, 789, 917, 1031 and 1108 cm^{-1} (Fig. 2a). According to Chandrasekhar [4], the bands in IR spectra of kaolin at wavenumber 540 cm^{-1} indicates the Al-O bond vibrations in $Al[O(OH)]_6$; at 789 and 914 cm^{-1} show the bond vibration of (Al-O)-H in $Al[O(OH)]_6$; at 430, 693, 752, 794, 1035, 1096 and 1114 cm^{-1} show the vibration of Si-O bonding in SiO_4 group.

The kaolin bands at wavenumber 429, 468, 697, 757, 917, 1031 and 1108 cm^{-1} do not appear in the infrared spectra of samples of ZSM-/12 (Fig. 2b). The disappearance of these bands indicate that the bonds in kaolin are disconnected to start forming new bonds. These data are supported by X-ray diffraction data on samples that high crystalline kaolin has turned into amorphous phase after hydrothermal process for 12 h as evidenced by the hump at 2θ 17-33°.

IR spectra of ZSM-5 is typically consist of five characteristic bands as shown in Fig. 2b. Band in 1221-1102 cm^{-1} region is resulted from the asymmetric stretching vibration of T-O-T bond; 796 cm^{-1} from the symmetric stretching vibration bond of T-O-T; 546 cm^{-1} from the framework vibration at pentacyl ring which is characteristic of the MFI-type zeolite structure and 450 cm^{-1} resulted from vibration of the T-O-T bending bond, where T is Si or Al atoms [18].

Based on Fig. 2b-d, the bands of infrared spectra at wavenumbers around 543 cm^{-1} from ZSM-5/12 h has the lowest intensity while the ZSM-5/24 sample has the highest intensity. This intensity is steady to the sample with crystallization time of 48 and 72 h (ZSM-5/48 and ZSM-5/72). According to Mohammed [19] the bands at 450 and 542 cm^{-1} are the characteristic of crystalline ZSM-5 which has the form of MFI structure [19]. The same result was reported by Somani *et al.* [20], who reported that the increasing band intensity at wavenumber of 550 cm^{-1} shows the concentration of the higher MFI structure. These results are consistent with XRD result of the four samples.

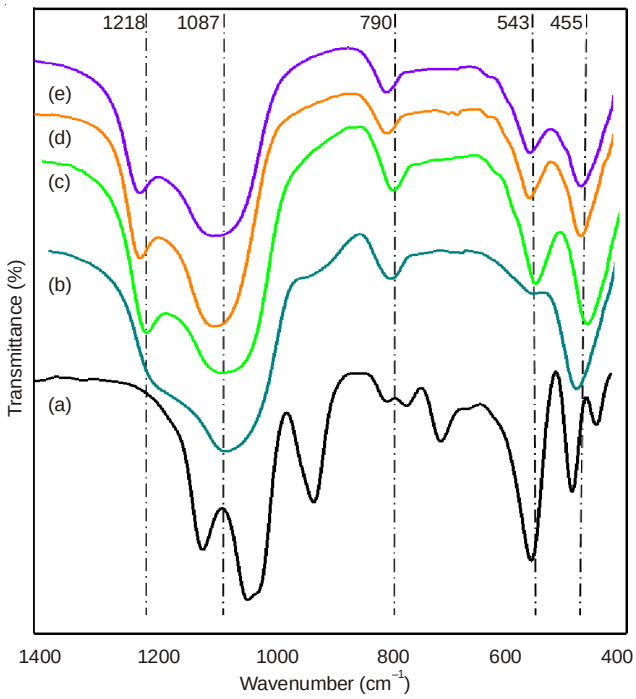

Fig. 2. Infrared spectra of (a) kaolin, (b) ZSM-5/12, (c) ZSM-5/24, (d) ZSM-5/48 and (e) ZSM-5/72

Infrared spectrum of ZSM-5/12 samples does not exhibit band at wavenumber 1218 cm^{-1}. According to Dong and Hun

[21] and Ali *et al.* [22], the band around 1229 cm^{-1} indicates the presence of three-dimensional shape of the channel pore. As described by Ali *et al.* [22] the bands at 1219 and 542 cm^{-1} are the characteristic bands of zeolite ZSM-5 which distinguish it with the others, due to the vibration of the MFI structure. Therefore, ZSM-5/12 samples has structure of ZSM-5 crystals, however the crystal are not perfect yet and is still in the early stages of nucleation.

Scanning electron microscopy-energy dispersive X-ray (SEM-EDX): Surface morphology of ZSM-5 samples are shown in Fig. 3. As seen in Fig. 3a, ZSM-5 sample with crystallization time 12 h has irregular morphology as fragments with diverse shapes. The particle sizes are around 0.57-2.57 µm. These results are consistent with X-ray diffraction data that the ZSM-5 samples with crystallization time 12 h has amorphous phase. However, the ZSM-5/24, ZSM-5/48 and ZSM-5/72 samples form the aggregate with a hexagonal crystal shape without sharp angle.

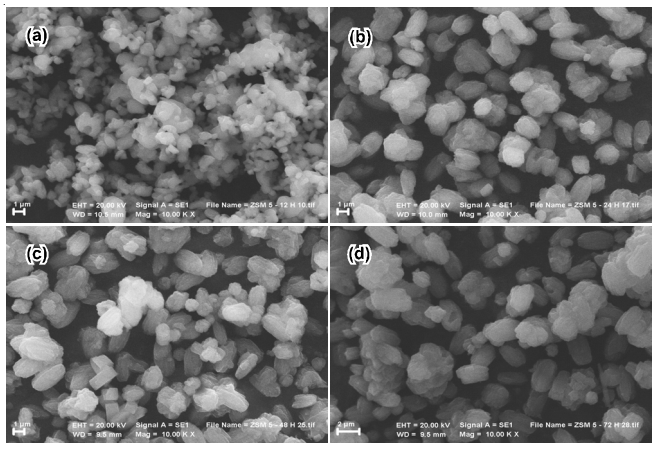

Fig. 3. Surface morphology of (a) ZSM-5/12, (b) ZSM-5/24, (c) ZSM-5/48 and (d) ZSM-5/72

Although the ZSM-5/24, ZSM-5/48 and ZSM-5/72 samples exhibits aggregates without sharp angle, the ZSM-5/24 sample still shows the crystal aggregates with sharper angle shape, indicated by square line (Fig. 4). These results are consistent with the characterization using XRD that ZSM-5/24 had the highest crystallinity. In addition, the samples with crystallization time of 48 and 72 h form aggregate with larger particles compare to the crystals around.

EDX measurement technique are performed to determine the composition of zeolite and Si/Al ratio. EDX results of the samples is shown in Table-2. All Si/Al ratio from the observed points are above 5,00. The EDX data confirm the data from XRD that all used precursor are completely form the ZSM-structure without formation of other phases.

TABLE-2
EDX RESULTS OF ZSM-5 SAMPLES WITH A VARIATION OF CRYSTALLIZATION TIME

Sample (h)	Content (%)					Particle size
	Si	Al	Na	O	Si/Al	
12	12.90	1.55	2.35	67.89	8.32	Small
24	18.69	1.97	2.77	71.82	9.49	Large
24	13.26	1.52	2.15	68.83	8.72	Small
48	18.89	3.24	3.53	68.89	5.83	Large
48	11.93	1.43	1.92	64.00	8.34	Small
72	19.57	3.41	3.76	69.70	5.74	Large
72	11.13	1.39	1.89	61.27	8.01	Small

Conclusion

ZSM-5 has been synthesized directly from kaolin without organic template with crystallization time of 12, 24, 48 and 72 h. Synthesis was carried out with kaolin precursor as main source of alumina and silica; NaOH as an agent of mineralization and source of Na^+ ions; silicalite as seed and LUDOX as a source of additional silica. The analysis using XRD and IR showed that the ZSM-5 began to be formed during the crystallization time of 12 h. ZSM-5 on the crystallization time of 24 h had the highest crystallinity and began to decrease at the crystallization time of 48 and 72 h. In addition, based on the SEM-EDX analysis of all samples shows the ratios of Si/Al between 5.74 to 9.49 with hexagonal shape, except for the sample at 12 h crystallization time which exhibited irregular shape.

ACKNOWLEDGEMENTS

The authors acknowledge to Directorate of Higher Education, Ministry of Education and Culture, Republic of Indonesia for financial support and Laboratory of Energy Studies ITS for technical support.

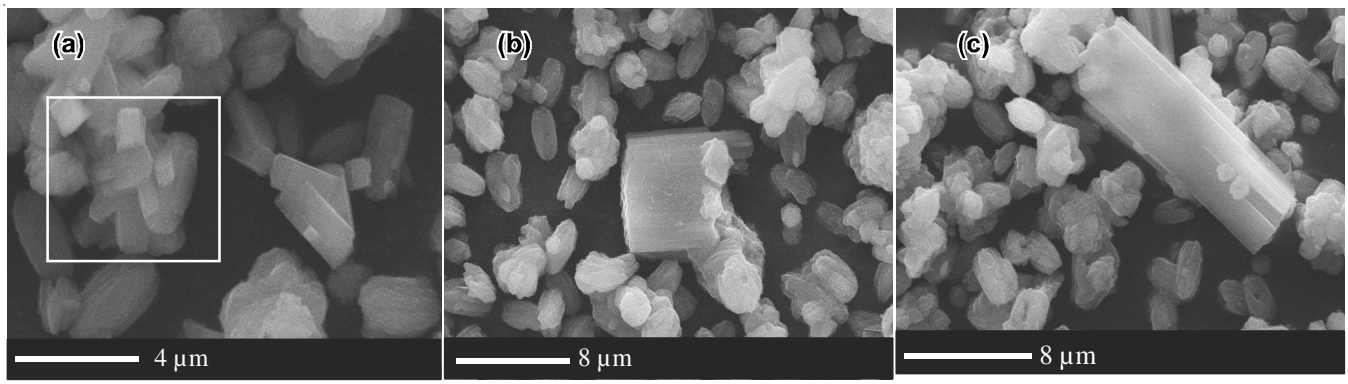

Fig. 4. Surface morphology of (a) ZSM-5/24, (b) ZSM-5/48 and (c) ZSM-5/72 samples

REFERENCES

1. Pusat Data dan Informasi Energi dan Sumber Daya Mineral, Indikator Energi dan Sumber Daya Mineral Indonesia (2011).
2. M.S. Prasad, K.J. Reid and H.H. Murray, *Appl. Clay Sci.*, **6**, 87 (1991).
3. H.H. Murray, Applied Clay Mineralogy Occurrences, Processing and Application of Kaolins, Bentonites, Palygorskite-Sepiolite and Common Clays, Elsevier's Science & Technology Right Department in Oxford, UK (2007).
4. S. Chandrasekhar, *Clay Miner.*, **31**, 253 (1996).
5. Y.A. Atta, Y.B. Jibril, O.B. Aderemi and S.S. Adefila, *Appl. Clay Sci.*, **61**, 8 (2012).
6. S. Bhatia, Zeolite Catalysis Principles and Applications, CRC Press, Boca Raton, Florida, pp. 171-209 (1990).
7. I. Lapides and H.L. Kallai, *Appl. Clay Sci.*, **35**, 94 (2007).
8. L.M. Mignoni, I.D. Petkowicz, F.R.C.N. Machado and B.C.S. Pergher, *Appl. Clay Sci.*, **41**, 99 (2008).
9. M. Khatamian and M. Irani, *J. Iranian Chem. Soc.*, **6**, 187 (2009).
10. H. Feng, C. Li and H. Shan, *Appl. Clay Sci.*, **42**, 439 (2009).
11. Y. Cheng, L.J. Wang, J.S. Li, Y.-C. Yang and X.-Y. Sun, *Mater. Lett.*, **59**, 3427 (2005).
12. S.D. Kim, H.S. Noh, W.J. Park and J.W. Kim, *Micropor. Mesopor. Mater.*, **92**, 181 (2006).
13. S.C. Cundy and A.P. Cox, *Micropor. Mesopor. Mater.*, **82**, 1 (2005).
14. D. Prasetyoko, N. Ayunanda, H. Fansuri, D. Hartanto and Z. Ramli, *ITB J. Sci.*, **44A**, 250 (2012).
15. J. Weithkamp and L. Puppe, Catalysis and Zeolite Fundamentals and Applicatons, Berlin, Germany (1999).
16. M. Alkan, C. Hopa, Z. Yilmaz and H. Guler, *Micropor. Mesopor. Mater.*, **86**, 176 (2005).
17. M.M.J. Treacy and J.B. Higgins, Collection of Stimulated XRD Powder Patterns for Zeolites, Elsevier, Amsterdam (2001).
18. T. Armaroli, L.J. Simon, M. Digne, T. Montanari, M. Bevilacqua, V. Valtchev, J. Patarin and G. Busca, *Appl. Catal. A*, **306**, 78 (2006).
19. R.M. Mohamed, H.M. Aly, M.F. El-Shahat and I.A. Ibrahim, *Micropor. Mesopor. Mater.*, **79**, 7 (2005).
20. O.G. Somani, A.L. Choudhari, B.S. Rao and S.P. Mirajkar, *Mater. Chem. Phys.*, **82**, 538 (2003).
21. D.J. Kim and H.S. Chung, *Appl. Clay Sci.*, **24**, 69 (2003).
22. I.O. Ali, A.M. Hassan, S.M. Shaaban and K.S. Soliman, *Sep. Purif. Technol.*, **83**, 38 (2011).