MJFAS MALAYSIAN JOURNAL OF FUNDAMENTAL AND APPLIED SCIENCES
PRINT ISSN: 2289-5981 | ONLINE ISSN: 2289-599X

RESEARCH ARTICLE

Effect of H_2O/SiO_2 molar ratio on direct synthesis of ZSM-5 from Bangka's kaolin without pretreatment

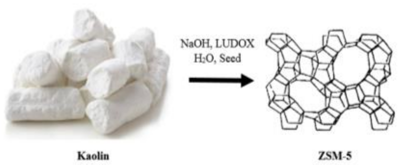
Djoko Hartanto[a,*], Rendy Muhamad Iqbal[a], Wahyu Erizky Shahbihi[a], Eko Santoso[a], Hamzah Fansuri[a], Ani Iryani[a,b]

[a] *Department of Chemistry, Faculty of Science, Institut Teknologi Sepuluh Nopember (ITS), Kampus ITS Sukolilo, Surabaya 60111, Indonesia*
[b] *Department of Chemistry, Pakuan University, Bogor, Indonesia*

* *Corresponding author: djokohar@its.ac.id*

Article history
Received 17 November 2017
Accepted 20 December 2017

Graphical abstract



Abstract

The influence of the molar ratio H_2O/SiO_2 in the synthesis directly from Bangka Belitung's Kaolin has been studied by performing synthesis of ZSM-5 with a variation of the molar ratio H_2O/SiO_2 is different at 15, 25, 30, and 35. Weighing 3.980 g Bangka's kaolin are added other material so obtained molar composition $10Na_2O$: $120SiO_2$: $2Al_2O_3$: 1800-4200H_2O, and 1% of silicalite seed, subsequent hydrothermal proccess of 175°C for 24 hours. The result of solids were analyzed by X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR) and SEM EDX to analyzed morphology of ZSM-5 crystal. The synthesis of ZSM-5 was directly optimum with molar ratio H_2O/SiO_2 of 30 having the highest cristalinity and largest crystal size of 59.44% and 3.795 μm, respectively.

Keywords**:** Kaolin, direct synthesis, ZSM-5, hydrothermal, zeolite

INTRODUCTION

Zeolite is aluminosilicat crystal that have pore and 3D framework, Based on their framework, International Zeolite Association (IZA) reported that zeolite have 218 framework (Kovo *et al*, 2009). Different type of zeolite framework has different application and properties.

Zeolite has many utilizate on industrial area, it has many advantages compared with others mineral because it has a uniform and regularity pore, strength acid site, and some type of zeolite has good thermal stability (Sun *et al*, 2007). Many researchers use zeolite as adsorben, ion exchanger, molecular siever and catalyst. Zeolite also has ability to solve waste water problem like active sludge material (Soraya *et al*, 2012). Beside natural zeolite, zeolite synthetic also developed by many researcher.

Zeolite Socony Mobil-5 (ZSM-5) is a type of zeolite that have pore channel on it's structure. Oil refinery and petrochemical industry use ZSM-5 as catalyst. In catalyst area, ZSM-5 called as heterogenous catalyst that have Brǿnsted and Lewis site. ZSM-5 use as catalyst for many reaction such as isomerisation, alkilation, catalytic cracking, epocsidation, hydrolisis, etc (Kovo *et al*, 2009). ZSM-5 can synthesized from raw material which has high contain of silica and alumina, such as kaolin (Wang *et al*, 2007 ; Hartanto *et al*, 2016), fly ash (Feng *et al*, 2009), rice husk (Prasetyoko *et al*, 2012), serpentin (Dong *et al*, 2003), and smektit (Abdmeziem *et al*, 1994). Synthesis of ZSM-5 from metakaolin as alumina source and silicate acid as silica source have been studied, activation kaolin at temperature from 600°C to 1100°C to form metakaolin (Pan *et al*, 2014). But, transformation to metakaolin need high temperature and increase cost of production. The utilizate source of silica and alumina from natural resource will decrease cost of synthesis and also temperature calcined.

Generally, ZSM-5 synthesized by hydrothermal from silica precusor, alumina, metal cation, and organic template. Conventional synthesis of zeolite using organic template like TPA^+ (Petushkov *et al*, 2011), utilization of tetrapropilamonium (TPA^+) has many problem such as difficult to degradation, high cost, and need of higher temperature to release the template (Dey *et al*, 2013). The high temperature of calcined might able to destroyed zeolite structure and decreasing crystalinity of ZSM-5. So, another promising way to synthesis of ZSM-5 is direct synthesis. Kim et al reported to direct synthesis of ZSM-5 with two step, first is nucleation at 190°C and continuesly by crystalization at 150-165°C (Kim *et al*, 2004). The advantages of direct synthesis is low calcined temperature, no treatment for source of silica and alumina (Kaolin). Synthesis of Zeolite use kaolin as source was reported by many researcher. Direct synthesis also use addition of ZSM-5 seed, after condensation and polymerisation reaction, percusor will form zeolite as well as their seed (Xue *et al*, 2012).

Direct synthesis of ZSM-5 without organic template was influenced by some factor like temperature, Si/Al molar ratio, and also H_2O/SiO_2 molar ratio. Generally, the higher temperature increase crystalinity, but every material has their limit. After optimum temperature, crystalinity of ZSM-5 would decrease, its caused higher temperature could broke zeolite structure (Dey *et al*, 2013 ;Hartanto *et al*, 2016). Another factor which influenced were H_2O/SiO_2 molar ratio. The amount of SiO_2 can controlled by addition of LUDOX as silica source and water play important thing in hydrothermal synthesis, its as place to crystal growth. But, if amount of water too much, proccess of synthesis would disturb by increasing amount of Na^+ and OH^- on proccess reaction. Its would disturb crystal formation and the product would has low crystalinity. In this study foccus to find optimum H_2O/SiO_2 molar ratio on ZSM-5 crystal formation.

EXPERIMENTAL

Materials

NaOH (Merck, 99%), LUDOX (Aldrich, 30 wt% of Si), Bangka Belitung's Kaolin (45,86% of SiO_2 and 22% of Al_2O3), ZSM-5 seed or Silicalite seed, and aquademineralization.

Synthesis of zeolite socony mobil-5 (ZSM-5)

In this research, ZSM-5 synthesized without organic template with different variation of H_2O/SiO_2 molar ratio : 15, 25, 30, and 35. The synthesis pathway follow a method was reported by Prasetyoko et al with $10Na_2O:120SiO_2:2Al_2O_3:1800H_2O$. 0.8 g of NaOH solute with water (Prasetyoko *et al*, 2012). Then, Kaolin added into NaOH solution under constant stirring until form white mixture. LUDOX was added into mixture and stirring during 8 hour (speed 400 rpm). The mixture left undisturbed condition during 12 hours at room temperature (aging). Next step, 0.085 (1 wt%) Silicalite seed added into the mixture and stiring for 30 minutes and then mixture moved into autoclave steel for hydrothermal proccess. Hydrothermal proccess under close condition at 175°C and the crystalization time is 24 hours. Solid product washed with aquadem and drying at 110°C during 12 hour.

Characterization of ZSM-5

The product of synthesis characterized by XRD JOEL JDX 3530 to determine crystal structure, Fourrier Transform Infrared (FTIR) Shimadzu Instrument Spectrum One 8400S to analyze function group on finger print area, and Scanning Electron Microscopy (SEM) FEI Inspect S25 and Energy Disspersive X-Ray (EDX) EDAX AMETEX to analyze morphology and compound of product, respectively.

Crystalinity of product also determine from difractogram, which calculated using equation :

Cristalinity (%) : Intensity of sample/Intensity of ZSM-5 Commercil x 100% (1)

RESULTS AND DISCUSSION

Direct synthesis of ZSM-5

Direct synthesis of ZSM-5 followed in this reaction (Xue *et al*, 2012) :

$$\text{Kaolin}_{(s)} + \text{NaOH}_{(aq)} + H_2O_{(l)} + SiO_{2\,(aq)} \longrightarrow \text{ZSM-5}_{(s)} \quad (2)$$

Reaction (Sun *et al*, 2007 ; Hartanto *et al*, 2016 ; Hartanto *et* al, 2016) use water as solvent and the condition was closed. In this hydrothermal synthesis would form Al-O-Si or T-O-T (T = Al or Si) by condentation reaction. After condentation reaction, its continuesly by polimerisation reaction and framework would follow ZSM-5 seed, the product will have same framework with ZSM-5 seed that followed Mordenite Framework Inverted (MFI) or researcher called product as ZSM-5.

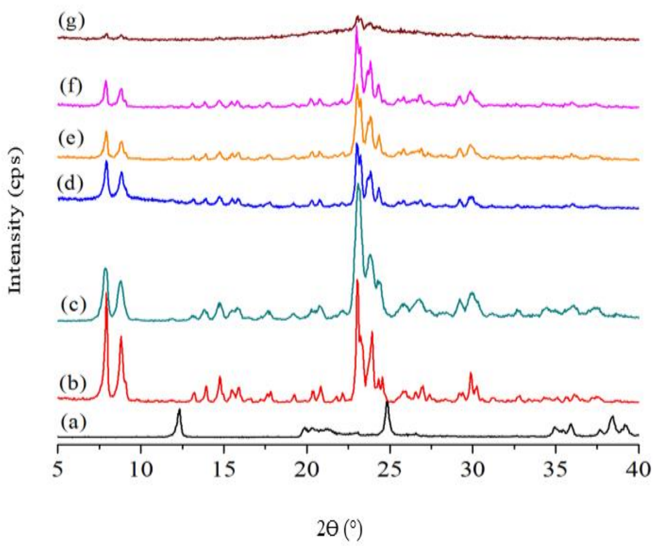


Fig. 1 XRD Pattern of (a) Kaolin (b) ZSM-5 Seed (c) ZSM-5 Commercil, ZSM-5 with H_2O/SiO_2 molar ratio (d) 15 (e) 25 (f) 30 (g) 35

Diffractogram of ZSM-5

ZSM-5 characterized by XRD at 2ϴ between 5-40°. Diffractogram of Bangka Belitung's kaolin (Fig. 1a) shown narrow peak at 2ϴ : 12.32, 19.87, 20.34, 24.85, 26.61, 34.95, 35.40, 35.91, 38.97, and 39.22°. This result match with kaolinit which has spesific peak at 2ϴ on 20.5° and 35-38.5°. Besides Kaolinit, Its possible Bangka Belitung's kaolin contain qwartz, iron, rutile, anatase, and also montmorilonite.

Diffractogram of ZSM-5 with molar ratio 35 (Fig. 1g) obtained amorph phase, its sign with appearing of hump at 17-33°, if compared with diffractogram of kaolin which has narrow peak, its indicate kaolin was soluted to form amorphous silica after hydrothermal proccess. Figure 1d-1f represent has same spesific peak with ZSM-5 comercil, It indicate kaolin was transform to ZSM-5 which has Mordenite Framework Invert (MFI) structure (Treacy *et al*, 2001 ; Hartanto *et al*, 2016) and narrow peak shown crystal of ZSM-5 was form

Crystalinity of ZSM-5 also studied and following equation 1 to calculate it. Tabel 1 showed result of crystalinity of ZSM-5 with different molar ratio.

Table 1 Crystalinity of ZSM-5 with different H_2O/SiO_2 molar ratio

H_2O/SiO_2	Crystalinity %
15	49.88
25	55.49
30	59.44
35	8.52

Based on Table 1, the highest crystalinity is ZSM-5 with molar ratio 30 and its reach 59.44%. Crystalinity of ZSM-5 increase with increasing amount of H_2O, but it decrease on molar ratio is 35. Its caused system of amorphous silica solution at high temperature should form silica crystal which has good stability, so kaolin can't transform to ZSM-5 and the product has low crystalinity of ZSM-5 (Prasetyoko *et al*, 2012).

Infrared spectrum of ZSM-5

Synthesize product characterized by FTIR to analyze functional group at finger print area. Figure 2 exhibit infrared spectrum from Kaolin, ZSM-5 seed, and also the synthesis product. Infrared spectrum of kaolin on Fig 2a showed spesific peak at 429, 468, 540, 697, 757, 789, 917, 1031, and 1108 cm^{-1}. Chandrasekar et al reported peak of kaolin, the wavenumber of 540 cm^{-1} indicate vibration of Al-O, 789 and 914 cm^{-1} represent of vibration (Al-O)-H, 430, 693, 752, 794, 1035, 1096, and 1114 cm^{-1} exhibit vibration of Si-O bonding on SiO_2 (Treacy *et al*, 2001). The wavenumber of 1115 and 1008 cm^{-1} obtained by stretching vibration from Si-O, the peak of 795 and 755 cm^{-1} shown vibration of Si-O-Si , 755 and 697 cm^{-1} is vibration of Al-O-H, 469 and 430 cm^{-1} indicate vibration of Si-O (Treacy *et al*, 2001). Figure 2 represent peak of kaolin at 429, 468, 697, 757, 917, 1031, and 1108 cm^{-1} did not appear on infrared spectrum of ZSM-5. Its indicate the bonding of kaolin have break and start to form new bond.

Infrared spectrum of ZSM-5 with different ratio shown in Fig 2(c-f), On spectrum appear 5 peak at 453, 545, 792, 1092 and 1222 cm^{-1}. Based on previous research, ZSM-5 has 5 spesific peak at 1221 and 1102 cm^{-1} from stretching asymmetric vibration of T-O-T, 796 cm^{-1} obtained by stretching symmetric vibration of T-O-T, 546 cm^{-1} showed framework vibration on pentacil ring and its characteristic of zeolite structure which has MFI type (Hartanto *et* al, 2016), and 450 cm^{-1} exhibit bending vibration from T-O-T bonding, where T is Si or Al. Ali et al reported that peak of 1090 cm^{-1} represent stretching asymmetric bending from SiO_4 tetrahedral, 545 cm^{-1} showed external bonding from tetrahedral with framework and 455 cm^{-1} represent bending vibration of Si-O bonding (Ali *et al*, 2003). Peak at 1224 cm^{-1} exhibit a pore that have three dimention channel (Dong *et al*, 2003), its caused by external stretching asymmetric vibration of TO_4 (Ali *et al*, 2003 ; Hartanto *et al*, 2016) . Based on data, it can concluded that the synthesize product is ZSM-5.

Based on Fig 2(c-f), peak of ZSM-5 at 543 cm^{-1} from sampel with molar ratio 15 has lowest transmintance and molar ratio 30 has highest transmintance value.

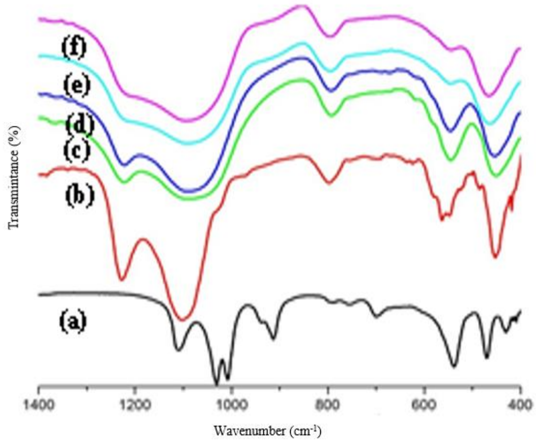


Fig. 2 Infrared spectrum of (a) Kaolin (b) ZSM-5 Seed, ZSM-5 with H_2O/SiO_2 molar ratio (c) 15 (d) 25 (e) 30 (f) 35

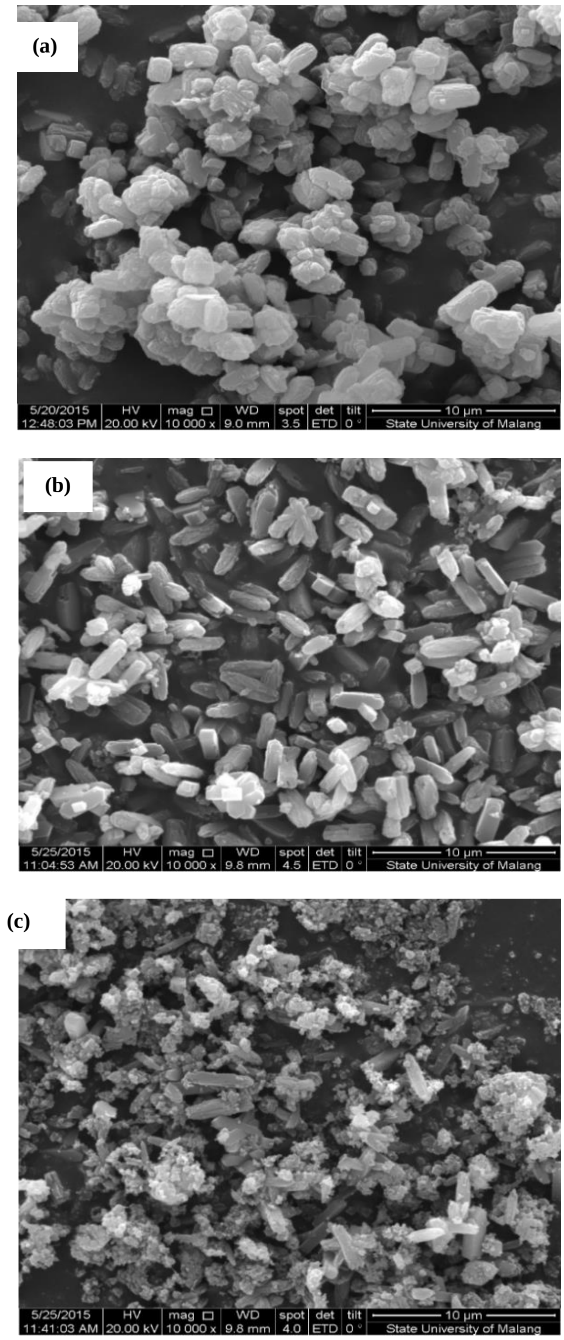


Fig. 3 Morphology of ZSM-5 with H_2O/SiO_2 molar ratio (a) 15 (b) 25 (c) 30

Morphology of ZSM-5

The observation of morphology ZSM-5 using Scanning Electron Microscopy(SEM). Morphology of ZSM-5 with different molar ratio shown by fig 3 (a-c). ZSM-5 with H_2O/SiO_2 molar ratio 15 shown aggregation of crystal, and shape of crystal has irregularity. For ZSM-5 with molar ratio 25 and 30 exhibit uniformity of crystal shape. Based on figure, the shape of crystal is hexagonal prism.

Hexagonal prism of crystal confirm that product is ZSM-5, SEM micrograph result support XRD and FTIR result. The shape of crystal influenced by crystalinity of ZSM-5. The higher amount of crystalinity will produce good hexagonal prism on SEM micrograph. Beside that, uniformity of crystal shape also important to analyze. For more detail shape and size of crystal, its shown by fig 4(a-c).

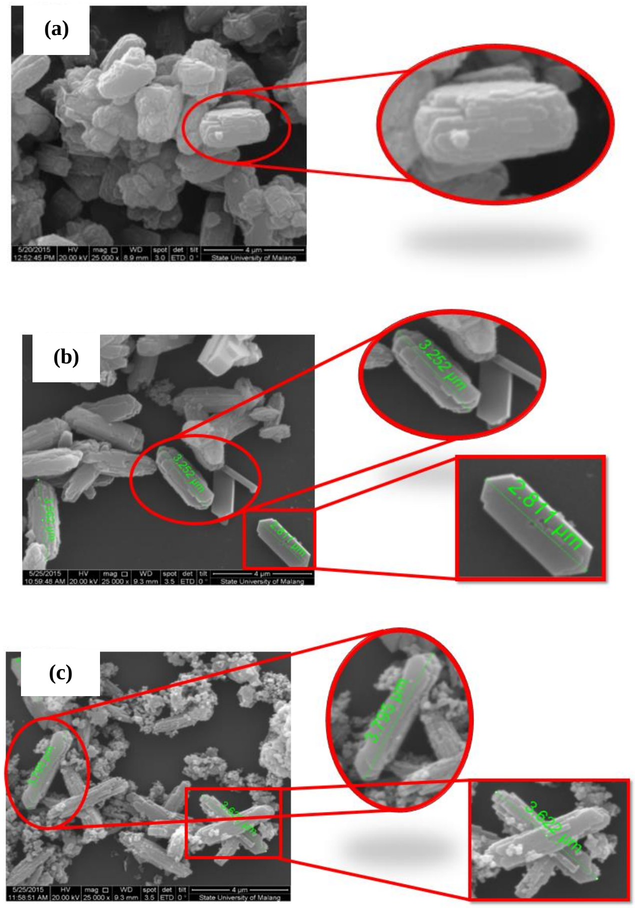


Fig 4 SEM Micrograph of ZSM-5 with H_2O/SiO_2 molar ratio (a) 15 (b) 25 (c) 30

Crystal size determined by SEM and the result shown by fig 4. ZSM-5 with molar ratio 15 has lowest of crystal size with the value is 2.684 µm, crystal size of ZSM-5 with molar ratio 25 is 3.562 µm, and ZSM-5 with molar ratio 30 has highest of crystal size and its value is 3.795 µm. Increasing of crystal size equals with increasing of crystalinity of ZSM-5.

The increasing size of crystal at higher H_2O/SiO_2 molar ratio (15-30), its caused on this condition could break percusor crystal and hydrothermal synthesis was transformed percusor to ZSM-5. The higher amount of H_2O would increasing crystal size, H_2O is place to growth of crystal, increasing amount of water can increase crystal size. But, the amount of water has their limit and if its amount too much, its will decrease crystalinity.

Energy Disspersive X-Ray (EDX) result

EDX analysis has purpose to determine compound of ZSM-5 product, the result shown by Table 2. ZSM-5 contain Si, Al, Na, and O with different percentage. The high compound of ZSM-5 product is oxygen and its percentage reach 66.16% on ZSM-5 with molar ratio 25. Si/Al ratio of ZSM-5 product also determined on Table and the result shown generally Si/Al for ZSM-5 product is 11.23, 11.70, and 11.41 for ZSM-5 with molar ratio 15, 25, and 30, respectively.

Table 2 Compound of ZSM-5 with different H_2O/SiO_2 molar ratio.

H_2O/SiO_2	Percentage %				
	Si	Al	Na	O	Si/Al
15	27.63	2.46	2.55	60.50	11.23
25	24.69	2.11	2.92	66.16	11.70
30	24.88	2.18	3.20	64.80	11.41

CONCLUSION

Bangka Belitung kaolin is promising natural resource as raw material to synthesis of ZSM-5. Where, its can use for direct synthesis and its product has different properties based on H_2O/SiO_2 molar ratio. The highest crystalinity is ZSM-5 with molar ratio 30 with the value 59.44%, its followed by molar ratio 25, 15, 35 and its value is 55.49; 49.88; 8.52%, respectively. The spectrum of infrared shown spesific peak at 1221 and 1102 cm^{-1} from stretching asymmetric vibration of T-O-T, 796 cm^{-1} obtained by stretching symmetric vibration of T-O-T, 546 cm^{-1} shown framework vibration on pentacil ring, and 450 cm^{-1} exhibit bending vibration from T-O-T bonding, 545 cm^{-1} shown external bonding from tetrahedral with framework and 455 cm^{-1} shown bending vibration of Si-O bonding. Peak at 1224 cm^{-1} represent a pore that have three dimention channel.

Observation of morphology from different H_2O/SiO_2 molar ratio represent different shape of crystal. ZSM-5 with H_2O/SiO_2 molar ratio 30 has shape like hexagonal prism and its also has highest crystal size with the value is 3.795 µm and followed by molar ratio 25 and 15 with value is 3.562 and 2.684 µm, respectively. EDX result shown Si/Al ratio for ZSM-5 with H_2O/SiO_2 molar ratio 15;25;30 is 11.23; 11.70; 11.41, respectively. From this work can concluded the optimum H_2O/SiO_2 molar ratio on direct synthesis of ZSM-5 is 30.

ACKNOWLEDGEMENT

This work was financially supported by the Ministry of Research, Technology and Higher Education of Indonesia under DRPM Grant.

REFERENCES

Abdmeziem, K., Siffert, B. 1994. Synthesis of large crystals of ZSM-5 zeolite from a smectite-type clay material. *Applied Clay Science* 8, 437-447

Ali, M. A., Brisdon, B., Thomas, W. J. 2003. Synthesis, Characterization and Catalytic Activity of ZSM-5 Zeolites Having Variable Silicon-to-Aluminium Ratios. *Applied Catalysis A: General* 252, 149-162.

Chandrasekhar, S., Pramada, P.N., 2004. Kaolin-based Zeolite Y, a precursor for cordierite ceramics. *Applied Clay Science* 27, 187-198

Cundy, C. S., Cox, P. A., 2003. The Hydrothermal Synthesis of Zeolites: History and Development from the Earliest Days to the Present Time. *J. Chemical Reviews* : 103. 663-702.

Dey, P. K., Ghosh, S., Naskar, K. M., 2013. Organic Template- Free Synthesis of ZSM-5 Zeolite Particles using Rice Husk Ash as Silica Source. *Ceramics International* 39, 2153- 2157.

Dong, J. K., Hun, S. C. 2003. Synthesis and characterization of ZSM-5 Zeolites from Serpentine *Applied Clay Science* 24, 60-77.

Hartanto, D., Yuan, L. S., Sari, S. M., Sugiarso, D., Murwani, I. K., Ersam, T., Nur, H., Prasetyoko, D., 2016, Can kaolin function as source of alumina in the synthesis of ZSM-5 without an organic template using a seeding technique?, *Malaysian Journal of Fundamental and Applied Sciences* 12 (2), 85-90

Hartanto, D., Saputro, O., Utomo, W. P., Rosyidah, A.,Sugiarso, D., Ersam, T., Nur, H., Prasetyoko, D., 2016, Synthesis of ZSM-5 directly from kaolin without organic template: Part-1: Effect of crystallization time, *Asian Journal of Chemistry* 28 (1), 211

Kim, S. D., Noh, S. H., Seong, K. H., Kim, W.J., 2004. Compositional and kinetic study on the rapid crystallization of ZSM-5 in the absence of organic template under stirring. *Microporous and Mesoporous* 72, 185-192.

Kovo, A. S., Hernandez, O., Holmes, S. M., 2009. Synthesis and characterization of zeolite Y and ZSM-5 from Nigerian Ahoko Kaolin using a novel, lower temperature. *Journal of Materials Chemistry*, 19(34), 6207-6212

Pan, F., Lu, X., Wang, Y., Chen, S., Wang, T, Yan, Y., 2014. Organic template-free synthesis of ZSM-5 zeolite from coal-series kaolinite. *Materials Letters* 115, 5–8

Petushkov, A., Yoon, S., Larsen, C. S., 2011. Synthesis of hierarchical nanocrystalline ZSM-5 with controlled particle size and mesoporisity. *Microporous and Mesoporous Materials* 137, 92-100.

Prasetyoko, D., Ayunanda, N., Fansuri, H., Hartanto, D., Ramli, Z. 2012. Phase transformation of rice husk ash in the synthesis of ZSM-5 without organic template. *ITB Journal Science*, 44A(3), 250-262

Soraya, D., Iryani, A., Mulyati, A. H., 2012. *Wastewater treatment at PT.X by active sludge (Pengolahan limbah cair PT. X secara lumpur aktif)*. Program Studi Kimia Fakultas Matematika dan Ilmu Pengetahuan Alam, Universitas Pakuan Bogor.

Treacy, M.M.J., Higgins, J.B. 2001. Collection of stimulated XRD powder patterns for zeolites. Amsterdam: Elsevier.

Wang, P., Shen, B., Shen, D., Peng, T., Gao, J. 2007. Synthesis of ZSM-5 zeolite from expanded perlite/kaolin and its catalytic performance for FCC naphtha aromatization. *Catalysis Communications* 8, 1452-1456.

Xue, T., Chen, T., Wang, Y.M., He, M.Y., 2012. Seed-induced synthesis of mesoporous ZSM-5 aggregates using tetrapropylammonium hydroxide as single template. *Microporous and Mesoporous Materials* 156, 97-105.