Est. 1984

ORIENTAL JOURNAL OF CHEMISTRY
An International Open Free Access, Peer Reviewed Research Journal

www.orientjchem.org

ISSN: 0970-020 X
CODEN: OJCHEG
2018, Vol. 34, No.(2):
Pg. 955-962

Synthesis of Co, Mo, Co-Mo and Mo-Co Catalysts, Supported on Mesoporous Silica-Alumina for Hydrocracking of α-Cellulose pyrolysis oil

MUHAMMAD FAJAR MARSUKI[1], WEGA TRISUNARYANTI[1]*,
IIP IZUL FALAH[1] and KARNA WIJAYA[1]

[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada Sekip Utara Bulaksumur, Yogyakarta, 55281, Indonesia.
*Corresponding author E-mail: wegats@ugm.ac.id

http://dx.doi.org/10.13005/ojc/340245

(Received: December 19, 2017; Accepted: January 15, 2018)

ABSTRACT

Cobalt, Molybdenum, Co-Mo and Mo-Co catalysts supported on mesoporous silica-alumina (MSA) were synthesized in this work. The MSA and catalysts were characterized by FTIR spectrometer, AAS, TEM, SAA and acidity test (pyridine adsorption). Their catalytic activity were investigated on hydrocracking of α-cellulose pyrolysis oil. The MSA had BET specific surface area of 52.01 m^2/g, total pore volume of 0.64 cm^3/g and pore diameter of 3.80 nm based on BJH desorption method. The results showed that hydrocracking of α-cellulose pyrolysis oil using Co/MSA, Mo/MSA, Co-Mo/MSA and Mo-Co/MSA catalysts was selective for acetic acid, 1-hydroxy-2-propanone and 2-furancarboxyldehide production. The highest amount of liquid product was obtained by using Co-Mo/MSA catalyst (82.13 wt.%).

Keywords: Silica alumina, Mesoporous, Catalysts, Hydrocracking, α-cellulose.

INTRODUCTION

Waste management is a great challenge to be solved in environmental technology. Waste processing by combustion will produce CO_2 emissions and cause air pollution. Conversion of waste into useful materials has become a concern to current researchers. The most studied waste conversion is conversion of biomass waste into useful materials such as bio-ethanol, bio-diesel, crude oil and others.

Biomass waste contains cellulose, hemicellulose and lignin. The biomass wastes can be converted into high-value chemicals. Production of chemicals such as food addictive, drugs, surfactants, organic solvents or fuels from biomass requires several conversion steps[1-4]. A way to convert biomass is through pyrolysis. Pyrolysis of biomass will produce tar, gaseous and liquid products (biomass pyrolysis oil). The biomass pyrolysis oil can be used for various purpose[5-8].

The biomass pyrolysis oil contains many oxidized organic compounds. Liquid product obtained from biomass pyrolysis should be upgraded. A way to upgrade the quality of biomass pyrolysis oil is hydrocracking on the liquid products using catalyst. Noble metal such as platinum (Pt) and palladium (Pd) can be used as catalyst in hydrocracking process[9-12]. However, the use of noble metals as catalyst is inefficient due to the cost of the noble metals. It makes metals on periods IV and V to be studied as catalyst. Bimetal catalysts from period IV and V had great activity for cracking hydrocarbon compounds (almost same with noble metals)[13-17].

The use of pure metal as catalyst in hydrocracking is ineffective because of the small metal surface area and possibility of sintering. These problems can be solved by supporting the metal in a porous material. Porous material provides a higher surface area which makes the metals to be distributed on its surface homogeneously and prevents the occurrence of sintering and agglomeration of metals. Futhermore, it can increase the catalyst active sites. [18-20]. Mesoporous support was more effective to accommodate high molecule weight and big molecule shape of feed fill inside the pores compare to that of microporous material[21]. Mesoporous supports such as SBA-15 and MCM-41 had been studied as a good mesoporous support of catalysts from period IV and V in hydrocracking of biomass[22-24].

Synthetic mesoporous materials are expensive and not easy to find them in the market. These synthetic materials can be replaced by the material made from natural sources. One of natural sources that can be used to synthesize mesoporous materials is lapindo mud that had occoured since 2006 in Sidoarjo, East Java. The lapindo mudflow sweped up to 180,000 m^3 of mud per day and contained a lot of silica and alumina[26-27]. This shows the potential of lapindo mud as a natural source in synthesizing mesoporous silica alumina. Mesoporous fabrication requires a template to regulate pore size during synthesis. The template is usually an organic sompound such as CTAB, HMI, and gelatin. The use of gelatin as a template in the synthesis of mesoporous silica alumina is still rare[28-29]. Gelatin is generally sourced from bone and skin of cow or pig[30-32]. However, religious reasons and mad cow disease make people begin to use marine animals as a source of gelatin[34-39]. Catfish that produced a lot of waste bone in the processing into food has not been widely utilized. Catfish bone waste can be used as a source of gelatin in the synthesis of mesoporous silica alumina.

In present study, the MSA was synthesized using silica and alumina extracted from Lapindo mud using gelatin extracted from catfish bone as a template. The MSA was impregnated with Co, Mo, Co-Mo, and Mo-Co metals. The catalysts were characterized and their activity were studied in hydrocracking process of α-cellulose pyrolysis oil.

EXPERIMENTAL

Materials

Catfish bone was collected from Tegalrejo Village, Central Java, Indonesia. Lapindo mud was collected from Sidoarjo Regency, East Java, Indonesia. Sodium hydroxide was purchased from VWR Chemicals. α-cellulose was purchased from Sigma-Aldrich. Acetic acid, pyridine, cobalt nitrate hexahydrate and ammonium heptamolybdate tetrahydrate were purchased from Merck & Co.

Synthesis of Mesoporous Silica Alumina

Silica and alumina were extracted from lapindo mud using 6 M NaOH and 6 M HCl solution at 90 °C, respectively. Catfish bone was prepared by soaking it in 0,1 NaOH solution for 24 h and 1 M HCl solution for 1 hours. Gelatin was extracted from the catfish bone using demineralized water at 80 °C. Catfish bone gelatin was dissolved in demineralized water at 40 °C and the gelatin solution was stirred for 30 minutes. The gelatin solution was then added with alumina mixture of gelatin-alumina was stirred for 30 minutes. On the other glass container, silica was added with demineralized water it was stirred for 30 minutes. The mixture of silica was then added with 1 M

CH_3COOH solution until the reaching pH 4. The mixture of silica was added into mixture of gelatin-alumina and stirred for the mixture was stirred for 24 h at room temperature. The formed gel solution was moved into autoclave and hydrothermally treated at 100 °C for 24 hours. The final product was filtered, washed with demineralized water, dried at 50 °C over a night and calcined at 500 °C for 5 h for removing of gelatin. The MSA was analyzed FTIR spectrometer, AAS, TEM, SAA and acidity test (pyridine adsorption).

Impregnation of Co and Mo on Mesoporous Silica Alumina

Cobalt and molybdenum metals were impregnated onto the MSA by wet impregnation method using $Co(NO_3)_2.6H_2O$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ salt solution and the mixture of MSA-salt solution was stirred for 24 hours. The mixture was dried at 70 °C for over a night. The catalyst was flowed by N_2 gas and calcined at 500 °C for 3 hours. The catalyst was then flowed by H_2 gas and heated at 450 °C for 3 h. Mo metal was impregnated onto the MSA followed by Co metal to produce CoMo/MSA catalyst and vice versa for MoCo/MSA catalyst. The catalysts were characterized by AAS, FTIR spectrometer and acidity test (pyridine adsorption).

Hydrocracking of α-Cellulose Pyrolysis Oil

α-cellulose was heated at 600 °C for 4 h under N_2 gas stream to produce α-cellulose pyrolysis oil. The liquid product obtained from pyrolysis of α-cellulose was hydrocracked at 600 °C for 2 h in a semi-batch stainless steel reactor (id: 4.5 cm, od: 4.8 cm, length: 30 cm) using catalysts synthesized in this study. Catalyst/α-cellulose pyrolysis oil ratio was 1/30. The liquid product from pyrolysis of α-cellulose and hydrocracking of α-cellulose pyrolysis oil were analyzed by GC-MS.

Acidity Test

The acidity of the MSA and catalysts were determined by flowing the pyridine vapor into the sample at vacuum condition for 24 h at room temperature. The acidity value of the MSA and catalysts were calculated using the following equation:

$$\text{Acidity Value} = \frac{\text{weight of sample after adsorption - weight of sample before adsorption}}{\text{weight of sample before adsorption} \times \text{Mr pyridine}}$$

Instrumentation

The functional groups of all sample were determined using fourier transform infrared spectroscopy (FTIR, Shimadzu Prestige-21) equipped with data station in the range of 400-400 cm^{-1} with α KBr disc technique. Surface area analyzer (SAA, Quantachrome NovaWin Series) was used to determine the surface parameters (surface area, pore volume, and pore diameter) of the MSA. The determination was based on physical adsorption of N_2 gas at batch temperature of 77.3 K. The MSA was degassed at 300 °C for 3 hours. The pore image was taken using transmission electron microscope (TEM, JEOL JEM-1400) at 120 kV accelerating voltage. The liquid produced by hydrocracking of α-cellulose pyrolysis oil was analyzed using gas chromatography-mass spectrometry (GC-MS, Shimadzu QP2010S) with a column length of 30 m, diameter of 0.25 mm, thickness of 0.25 µm, temperature of 60-310 °C, Helium gas as carrier gas, and acceleration voltage of 70 Ev.

RESULTS AND DISCUSSION

Characterization of Mesoporous Silica Alumina

Figur 1 showes FTIR spectra of MSA before and after calcination. Before calcination (see Fig. 1a), FTIR spectra of MSA had absorption peak at 3449 cm^{-1} which corresponds to stretching vibration of O-H. FTIR spectra of MSA had also absorption peak at 1003 cm^{-1} which refers to asymmetric stretching vibration of T-O (T = Si or Al). Absorption peak at 718 cm^{-1} that appeared on FTIR spectra of MSA corresponds to symmetric stretching vibration of T-O. FTIR spectra of MSA had absorption peak at 586 cm^{-1} which corresponds to double ring vibration. Absorption peak at 424 cm^{-1} corresponds to bending vibration of T-O[40-42]. After calcination, absorption peaks which corresponded to symmetric stretching vibration of T-O and bending vibration of T-O on FTIR spectra of MSA (see Fig. 1b) were shifted to 725 cm^{-1} and 455 cm^{-1}, respectively.

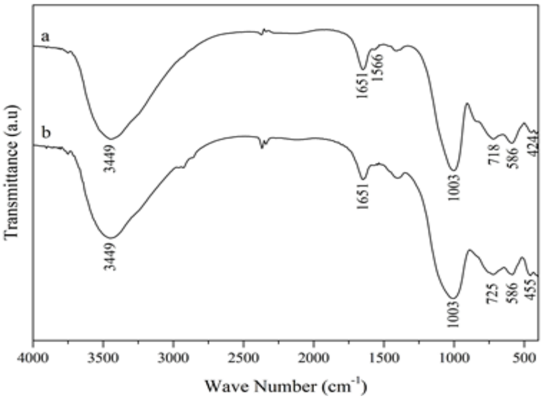

Fig. 1. FTIR spectra of MSA (a) before calcination and (b) after calcination

AAS analysis results in Table 1 shows that the real Si/Al ratios of MSA was 0.69. The acidity of the MSA and the catalysts was determined by introducing pyridine vapor on the MSA and the catalysts at vacuum condition for 24 hours. Increasing of the MSA and the catalysts weight was used to measure their acidity value. Table 1 shows that acidity value (amount of pyridine absorbed by acid sites) of the MSA was about 4.82 mmol/g. N_2 adsorption-desorption isotherm of MSA was showes in Fig. 2. The MSA showed type IV isotherm that indicated formation of mesoporous on the MSA.

Table 1: Properties of MSA

Properties	Value
Si/Al Ratio (AAS)	0.69
Acidity Value (Pyridine Adsorption)	4.82 mmol/g
Surface Area (BET Method)	52.01 m^2/g
Total Volume	0.64 cm^3/g
Pore Diameter (BJH Desorption Method)	3.80 nm

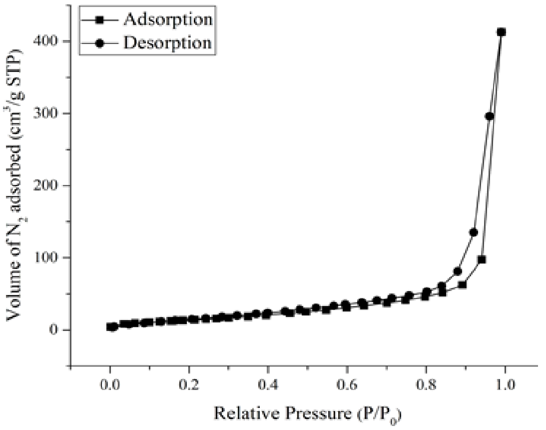

Fig. 2. Adsorption-desorption isotherm of MSA

Figure 3 shows TEM micrograph of the MSA. TEM result indicated that the MSA had a wormhole-like pore structure. This result was similar to those of the TEM micrograph of MSA that were synthesized on previous work[28-29,43]. The pore size of MSA was not uniform because the gelatin used a template in synthesis of MSA had a wide molecular weight distribution range.

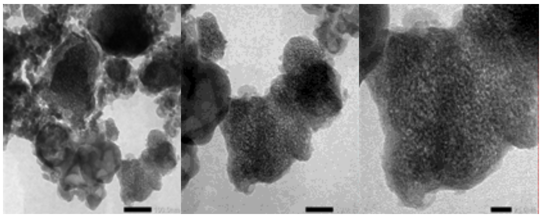

Fig. 3. TEM micrographs of MSA

Table 2: AAS and acidity test results of MSA

Catalyst	Acidity Value (mmol/g)	Co (%)	Mo (%)
Co/MSA	15.46	1.66	0
Mo/MSA	15.61	0	1.77
CoMo/MSA	16.58	2.12	1.65
MoCo/MSA	17.28	1.53	1.88

The metal content and acidity of catalysts were shown in Table 2. The Co/MSA contained 1.66% of Co metal. This result was almost equal to the MoCo/MSA that contained 1.53% of Co metal. However, the CoMo/MSA had more amount of Co metal (2.12%) than the others. The Mo/MSA contained 1.77% of Mo metal. The amount of Mo metal impregnated in CoMo/MSA and MoCo/MSA was 1.65% and 1.88%, respectively. The amount of Co and Mo metals impregnated on the MSA was less than 2% (initially amount of metal impregnated onto the MSA). Co and Mo salts could not be fully impregnated into MSA pore because Co and Mo salts also had interaction with the solvent. The interaction between salt and MSA could be resisted by interaction between salt and the solvent.

The acidity of MSA after impregnated with Co and Mo metals increased up to three times (more than 15 mmol/g) of the initial acidity of MSA

(4.82 mmol/g). The acidity value of catalysts are shown in Table 2. Co and Mo metals have empty d-orbitals which could be Lewis acid site. The empty d-orbitals on Co and Mo metals could accept free electron pair of nitrogen atoms on pyridine ring compound[13]. This caused the acidity value of MSA increased significantly after impregnation of Co and Mo metals. The increasing of acidity of the catalysts was expected to increase their activity in hydrocracking of α-cellulose pyrolysis oil.

Acitivity of Catalysts

α-cellulose pyrolysis oil was physically dark brown and thick. Pyrolysis conducted in this research succeeded in converting α-cellulose into liquid product as much as 40.68%. α-cellulose pyrolysis oil contained furan, ketones, alcohols, aldehydes and carboxylic acids. Five main components of the α-cellulose pyrolysis oil were 2-furankarboxyldehide (32.13%), 1-acetyloxy-2-butanone (10.73%), acetic acid (10.23%), 1-hydroxy-2-propanone (8.60%) and 2-hydroxy-3-methyl-2-cyclopenten-1-one (8.26%).

Hydrocracking of α-cellulose pyrolysis oil was carried out with and without (thermal hydrocracking) catalysts. Hydrocracking without catalyst or thermal hydrocracking was carried out to prove that the catalysts synthesized in this study had catalytic activity in the hydrocracking of α-cellulose pyrolysis oil. Thermal hydrocracking of α-cellulose pyrolysis oil produced the lowest liquid product conversion and it was dominated by the gas product as shown in Fig. 4. High temperatures cause homolysis toward organic compound. The homolysis of organic compound forms free radical that could bind free radical of hydrogen to form short chain carbon compound. In addition, the radical compound could also bind other radical compound to form a short chain carbon compound. The short chain carbon compound would tend to be in the gas phase[30-31,44]. The hydrocracking of α-cellulose pyrolysis oil using the catalyst produced greater liquid product conversion than that of the thermal hydrocracking. The utilization of catalysts in the hydrocracking of α-cellulose pyrolysis oil increased the the amount of liquid product and decreased the amount of gas product. This result indicated that the synthesized catalysts showed activity as expected.

Table 3: Composition of α-cellulose pyrolysis oil

Yield (%)	Compound	
0.51	2-hydroxy-3-methyl-1,4-naphthalenedione	$C_{11}H_8O_3$
0.19	acetaldehyde	C_2H_4O
4.23	acetone	C_3H_6O
1.03	acetic acid ethenyl ester	$C_4H_6O_2$
1.59	formic acid	CH_2O_2
2.16	2-butanone	C_4H_8O
10.23	acetic acid	$C_2H_4O_2$
8.60	1-hydroxy-2-propanone	$C_3H_6O_2$
2.86	propanoic acid	$C_3H_6O_2$
1.31	methyl oxirane	C_3H_6O
2.99	butanoic acid	$C_4H_8O_2$
32.13	2-furancarboxyldehide	$C_5H_5O_2$
0.65	1-acetyloxy-2-propanone	$C_5H_8O_3$
0.55	2-methyl-2-cyclopenten-1-one	C_6H_8O
1.01	1-(2-furanyl)-ethanone	$C_6H_6O_2$
0.16	1,2-butanolide	$C_4H_6O_2$
10.73	1-acetyloxy-2-butanone	$C_6H_{10}O_3$
7.92	5-methyl-2-furancarboxyldehide	$C_6H_6O_2$
1.52	3-methyl-2-cyclopenten-1-one	C_6H_8O
8.26	2-hydroxy-3-methyl-2-cyclopenten-1-one	$C_6H_8O_2$
1.36	2,2-dimethyl-butanoic acid	$C_6H_{12}O_2$

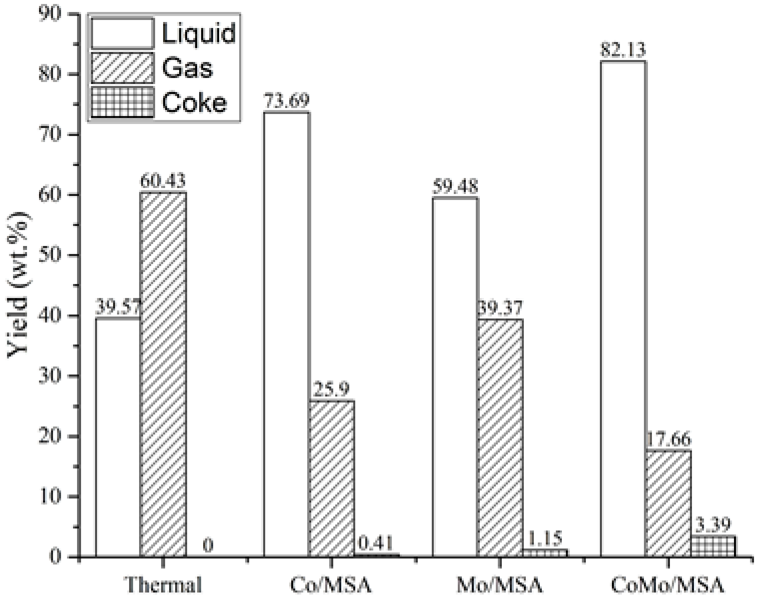

Fig. 4. Product distribution of hydrocracking of α-cellulose pyrolysis oil

The highest total conversion of α-cellulose pyrolysis oil was obtained from the hydrocracking using Co/MSA catalyst and the lowest total conversion was obtained from the hydrocracking using Mo/MSA catalyst. This phenomenon occured because all of 4d-orbitals on molybdenum had been filled with unpaired electrons making it was difficult to bind the hydrogen radicals produced from homolysis of hydrogen gas. However, cobalt had only three half-filled 3d-orbitals making it was easier to bind hydrogen radicals from homolysis of hydrogen gas than molybdenum.

The amount of liquid product obtained from hydrocracking using CoMo/MSA and MoCo/MSA catalysts was higher than Co/MSA and Mo/MSA catalysts. This phenomenon was caused by the synergetic effect between Co and Mo metals. Mo metal had previously been explained that it was difficult to bind hydrogen radical in hydrocracking reaction. It made the molybdenum had lower activity than cobalt. However, the use of molybdenum as a promoter could increase the activity of cobalt. It made the catalytic activity of CoMo/MSA and MoCo/MSA higher than Co/MSA and Mo/MSA.

The Co metal had a smaller atomic radius (2 Å) compared to molybdenum (2.17 Å). If Co metal was previously impregnated into the MSA, the cobalt would coat the entire surface of the cobalt. It made only a half of the cobalt that could interact with the reactants. However, if the metal Mo is previously impregnated into the MSA, cobalt would only coat a half of the surface of Mo metal. It means that all of Co and Mo metals could interact with the reactants. The activity of catalyst would be greater, if all of cobalt could interact with the reactants. This explanation corresponded with the fact that the CoMo/MSA had higher total conversion of α-cellulose pyrolysis oil than MoCo/MSA in this study.

The liquid product obtained from hydrocracking of α-cellulose pyrolysis oil was physically yellow and dilute. It was different from the α-cellulose pyrolysis oil which was dark brown and thick. largest amount of compound produced by the thermal hydrocracking was 1,2-ethanediol. The result was different from the hydrocracking of α-cellulose pyrolysis oil using the catalysts. The liquid products produced in hydrocracking of α-cellulose pyrolysis oil using the catalysts did not consist of 1,2-etanadiol, but they consist of acetic acid, 1-hydroxy-2-propanone and 2 furancarboxyldehide as the main compounds. The result proved that the catalysts synthesized in this study had activity in hydrocracking of α-cellulose pyrolysis oil.

Table 4: Contents of liquid product from hydrocracking of α-cellulose pyrolysis oil

Catalyst	Yield (wt.%)			
	1,2-ethanadiol ($C_2H_6O_2$)	acetic acid ($C_2H_4O_2$)	1-hydroxy-2-propanone ($C_3H_6O_2$)	2-furancarboxyldehide ($C_5H_5O_2$)
Thermal	19.13	7.04	4.70	1.99
Co/MSA	-	32.57	12.34	9.54
Mo/MSA	-	16.09	11.10	14.89
CoMo/MSA	-	24.37	13.19	17.62
MoCo/MSA	-	16.32	15.49	6.66

CONCLUSION

The MSA synthesized in this study presented BET specific surface area of 52.01 m^2/g, total pore volume of 0.64 cm^3/g and pore diameter of 3.80 nm based on BJH desorption method. Acidity value of MSA increased up to three times of the initial acidity after impregnation of Co and Mo metals. Hydrocracking of α-cellulose pyrolysis oil produced highest amount of liquid product by using CoMo/MSA catalystand it was about 82.13 wt.%. Main compounds obtained from hydrocracking using the catalysts were acetic acid, 1-hydroxy-2-propanone and 2-furancarboxyldehide.

ACKNOWLEDGEMENT

This research was conducted under the research grant of PUPT 2017 Universitas Gadjah Mada. The authors therefore thank to the Indonesian Ministry of Research, Technology, and Higher Education for the financial support (Contract number: 2454/UN1.P.III/DIT-LIT/LT/2017).

REFERENCES

1. Klass, D. L. *J. Environ. Qual.* **2004**, *1*, 193–212.
2. Maschio, G.; Koufopanos, C.; Lucchesi, A. *Bioresour. Technol.* **1992**, *42*, 219–231.
3. Collard, F. X.; Blin, J. *Renew. Sustain. Energy Rev.* **2014**, *38*, 594–608.
4. Stefanidis, S. D.; Kalogiannis, K. G.; Iliopoulou, E. F.; Michailof, C. M.; Pilavachi, P. A.; Lappas, A. A. *J. Anal. Appl. Pyrolysis.* **2014**, *105*, 143–150.
5. Sallevelt, J. L. H. P.; Pozarlik, A. K.; Brem, G. *Energy Convers. Manag.* **2016**, *127*, 504–514.
6. Van De Beld, B.; Holle, E.; Florijn, J. *Appl. Energy.* **2013**, *102*, 190–197.
7. Han, Y.; Stankovikj, F.; Garcia-Perez, M. *Fuel Process. Technol.* **2017**, *159*, 328–339.
8. Krutof, A.; Hawboldt, K. *Renew. Sustain. Energy Rev.* **2016**, *59*, 406–419.
9. Regali, F.; Boutonnet, M.; Järås, S. *Catal. Today.* **2013**, *214*, 12–18.
10. Gutierrez, A.; Arandes, J. M.; Castano, P.; Olazar, M.; Bilbao, J. E. *Energy and Fuels.* **2012**, *26*, 5897–5904.
11. Gutiérrez, A.; Arandes, J. M.; Castaño, P.; Olazar, M.; Bilbao, J. *Fuel.* **2012**, *94*, 504–515.
12. Grilc, M.; Likozar, B.; Levec, J. *Appl. Catal. B Environ.* **2014**, *150*, 275–287.
13. Sriningsih, W.; Saerodji, M. G.; Trisunaryanti, W.; Triyono; Armunanto, R.; Falah, I. I. *Procedia Environ. Sci.* **2014**, *20*, 215–224.
14. Upare, D. P.; Park, S.; Kim, M. S.; Jeon, Y. P.; Kim, J.; Lee, D.; Lee, J.; Chang, H.; Choi, S.; Choi, W.; Park, Y. K.; Lee, C. W. *J. Ind. Eng. Chem.* **2017**, *46*, 356–363.
15. Kadarwati, S.; Hu, X.; Gunawan, R.; Westerhof, R.; Gholizadeh, M.; Hasan, M. D. M.; Li, C. Z. *Fuel Process. Technol.* **2017**, *155*, 261–268.
16. Nava, R.; Pawelec, B.; Castaño, P.; Álvarez-Galván, M. C.; Loricera, C. V.; Fierro, J. L. G.

Appl. Catal. B Environ. **2009**, *92*, 154–167.

17. Chen, W.; Mauge, F.; Van Gestel, J.; Nie, H.; Li, D.; Long, X. *J. Catal.* **2013**, *304*, 47–62.
18. Muthu Kumaran, G.; Garg, S.; Soni, K.; Kumar, M.; Gupta, J. K.; Sharma, L. D.; Rama Rao, K. S.; Murali Dhar, G. *Microporous Mesoporous Mater.* **2008**, *114*, 103–109.
19. Opalka, S. M.; Zhu, T. *Microporous Mesoporous Mater.* **2016**, *222*, 256–270.
20. Lang, N.; Tuel, A. *Microporous Mesoporous Mater.* **2005**, *77*, 147–157.
21. Meynen, V.; Cool, P.; Vansant, E. F. *Microporous Mesoporous Mater.* **2009**, *125*, 170–223.
22. Lu, M.; Liu, X.; Li, Y.; Nie, Y.; Lu, X.; Deng, D.; Xie, Q.; Ji, J. *J. Renew. Sustain. Energy.* **2016**, *8*, 1–12.
23. Khoshbin, R.; Karimzadeh, R. *Adv. Powder Technol.* **2017**, *28*, 973–982.
24. Looi, P. Y.; Mohamed, A. R.; Tye, C. T. *Chem. Eng. J.* **2012**, *181*, 717–724.
25. Twaiq, F. A.; Mohamed, A. R.; Bhatia, S. *Microporous Mesoporous Mater.* **2003**, *64*, 95–107.
26. Abidin, H. Z.; Davies, R. J.; Kusuma, M. A.; Andreas, H.; Deguchi, T. *Environ. Geol.* **2009**, *57*, 833–844.
27. Jalil, A. A.; Triwahyono, S.; Adam, S. H.; Rahim, N. D.; Aziz, M. A. A.; Hairom, N. H. H.; Razali, N. A. M.; Abidin, M. A. Z.; Mohamadiah, M. K. A. *J. Hazard. Mater.* **2010**, *181*, 755–762.
28. Masykuroh, A.; Trisunaryanti, W.; Falah, I. I.; Sutarno. *Int. J. ChemTech Res.* **2016**, *9*, 598–606.
29. Trisunaryanti, W.; Lisna, P. S.; Kartini, I.; Sutarno; Falah, I. I.; Triyono. *Asian J. Chem.* **2016**, *28*, 996–1000.
30. Pongsendana, M.; Trisunaryanti, W.; Artanti, F. W.; Falah, I. I.; Sutarno. *Korean J. Chem. Eng.* **2017**, *34*, 1–6.
31. Trisunaryanti, W.; Fallah, I. I.; Ningtyas, A.; Swasdika, F.; Ratna, D. A. *Int. J. ChemTech Res.* **2016**, *9*, 96–103.
32. Ulfa, M.; Trisunaryanti, W.; Falah, I. I.; Kartini, I. *IOSR J. Appl. Chem.* **2015**, *8*, 57–63.
33. Benjakul, S.; Oungbho, K.; Visessanguan, W.; Thiansilakul, Y.; Roytrakul, S. *Food Chem.* **2009**, *116*, 445–451.
34. Wangtueai, S.; Noomhorm, A. *LWT - Food Sci. Technol.* **2009**, *42*, 825–834.
35. Al-Saidi, G. S.; Al-Alawi, A.; Rahman, M. S.; Guizani, N. *Int. Food Res. J.* **2012**, *19*, 1167–1173.
36. Tabarestani, H. S.; Maghsoudlou, Y.; Motamedzadegan, A.; Sadeghi Mahoonak, A. R. *Bioresour. Technol.* **2010**, *101*, 6207–6214.
37. Karim, A. A.; Bhat, R. *Food Hydrocoll.* **2009**, *23*, 563–576.
38. Nagarajan, M.; Benjakul, S.; Prodpran, T.; Songtipya, P.; Kishimura, H. *Food Hydrocoll.* **2012**, *29*, 389–397.
39. Sinthusamran, S.; Benjakul, S.; Kishimura, H. *Food Chem.* **2014**, *152*, 276–284.
40. Al Mubarok, M. A. S.; As Silmi, N. A.; Trisunaryanti, W.; Sutarno. *Int. J. Acad. Sci. Res.* **2014**, *2*, 26–30.
41. Xu, B.; Yang, Y.; Xu, Y.; Han, B.; Wang, Y.; Liu, X.; Yan, Z. *Microporous Mesoporous Mater.* **2017**, *238*, 84–89.
42. Robson, H.; Lillerud, K. P. *Verified Syntheses of Zeolitic Materials.* Elsevier, Amsterdam., **2001**.
43. Nurmalasari; Trisunaryanti, W.; Sutarno; Falah, I. I. *Int. J. ChemTech Res.* **2016**, *9*, 607–614.
44. Salim, I.; Trisunaryanti, W.; Triyono; Arryanto, Y. *Int. J. ChemTech Res.* **2016**, *9*, 492–500.