

Synthesis of ZSM-5 zeolite from coal fly ash and rice husk: characterization and application for partial oxidation of methane to methanol

Y K Krisnandi¹, F M Yanti^{1,2} and S D S Murti²

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia

²Agency for Assessment and Application of Technology, Jl. M.H Thamrin 8, Jakarta, Indonesia

Corresponding author's e-mail: yuni.krisnandi@sci.ui.ac.id

Abstract. Indonesian fly ash ($\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio = 3.59) was used together with rice husk (SiO_2 92%) as raw material for mesoporous ZSM-5 zeolite synthesis. Prior being used, coal fly ash and rice husk were subjected to pre-treatment in order to extract silicate (SiO_4^{4-}) and aluminate (AlO_4^{5-}) and to remove the impurities. Then the ZSM-5 zeolite were synthesized through hydrothermal treatment using two types of templates (TPAOH and PDDA). The as-synthesized ZSM-5 was characterized using FTIR, XRD, SEM-EDX, and BET. The result of FTIR showed peaks at $1250\text{-}950\text{ cm}^{-1}$ ($\nu_{\text{asymmetric T-O}}$), $820\text{-}650\text{ cm}^{-1}$ ($\nu_{\text{symmetric T-O}}$), and at $650\text{-}500\text{ cm}^{-1}$ confirming the presence of the five number ring of the pentasil structure. The result of XRD showed the appearance of certain peaks in the position 2 theta between $7\text{-}9^\circ$ and $22\text{-}25^\circ$ indicative of ZSM-5 structure, but also showed the pattern of low intensity magnetite and hematite. The SEM image showed the rough surface of hexagonal crystals from ZSM-5 structure, indicative of mesoporosity in the structure. EDX result showed Si/Al ratio of 20, while surface area analysis gave SA of 43.16. The ZSM-5 zeolites then was modified with cobalt oxide through impregnation method. The catalytic activity as heterogeneous catalysts in partial oxidation of methane was tested. The result showed that hence the catalytic activity of ZSM-5 and Co/ZSM-5 from fly ash and rice husk were still inferior compared to the pro-analysis sourced-counterpart, they were potential to be used as catalyst in the partial oxidation of methane to methanol.

Keyword: coal fly ash, rice husk ash, synthesis of ZSM-5, partial oxidation, methane to methanol

1. Introduction

Coal is the world's most abundant and widely distributed fossil fuel, with global proven reserves totaling nearly 1000 billion [1]. The major problem in coal-fired power generation is that the plenty of solid waste so-called fly ash (of about 30% of raw coal) is produced [2]. Previously, almost all the fly ash was disposed by landfill, which became increasingly expensive and caused an environmental problem. Therefore, research on utilization of the by-product coal fly ash requires an urgent attention. This fly ash contains at least 50% of alumina and silicate which is composed of amorphous solid and hollow sphere [3]. Due to these similarities in the composition between coal fly ash and zeolite, coal fly ash has been viewed as a potential candidate for conversion to zeolite [4].



Chareopanich *et al.* [5] has been success to synthesis of ZSM-5 zeolite from lignite coal fly ash and rice husk ash which is produced microporous ZSM-5 zeolite. Microporous zeolite makes large molecules cannot react effectively over these microporous materials because of the limitation of their small pore sized [6]. Panpa *et al.* [7] has been success to synthesis of ZSM-5 from rice husk. Mohammed *et al.* [8] also has been success to synthesis and characterization of ZSM-5 zeolite from rice husk ash and their implication for photocatalytic degradation catalyst.

The focus of this work is the synthesis of ZSM-5 zeolite using fly ash the main raw material. However, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio in the raw fly ash is too low for ZSM-5 synthesis ($\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio = 3.59). In order to obtain the appropriate $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio, the silicate was added to adjust the mole ratio of fly ash. From economic point of view, the silicate prepared from rice husk ash was used instead of commercial ones because there is abundant supply of rice husk in Indonesia.

2. Materials and methods

2.1. Materials

The materials used were: Coal Fly Ash from Paiton, Indonesia, rice husk from Bogor, Indonesia, sodium hydroxide (NaOH) pellet, Chloride acid (HCl) 1M, Tetrapropylammonium hydroxide, TPAOH 1M (Sigma Aldrich), Poly Diallyl Dimethyl Ammonium Chloride (PDMA 35%) (Aldrich), Cobalt (II) Nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (Sigma Aldrich), methane gas (99.99% BOC), N_2 gas (99.99% UHP) and deionized water.

2.2. Pretreatment of coal fly ash and rice husk ash

Coal fly ash was dried and sieved using a 200 mesh sieve, and then activated in a furnace at a temperature of 800°C for 2 hours, then refluxed with 1M HCl for 3 hours at 90°C . After this, the mixture was washed with distilled water to pH neutral. Then the product was filtered with filter paper, and then sample was dried in an oven with a temperature of 105°C for 6 hours.

Rice husk sample was washed, then dried in an oven at 105°C for 1 hour, then the sample was crushed and sieved 60 mesh, then burned with a furnace at 700°C for 4 hours, then characterized by AAS, FTIR and XRD.

2.3. Synthesis of ZSM-5

Synthesis of ZSM-5 was prepared with a molar ratio: $12\text{NaOH} : 30\text{SiO}_2 : 0.75\text{Al}_2\text{O}_3 : 6\text{TPAOH} : 1800\text{H}_2\text{O}$. In this experiments, 2.0286 g of coal fly ash was mixed with 30 mL of 0.4 M NaOH solution (mixture A) at 100°C . Then 5.7187 g rice husk ash was added with 70 mL of 0.4 M NaOH and then stirred at 100°C (mixture B). Furthermore, mixture's B was slowly added to the mixture A, then 4.0552 g TPAOH was added to the mixture, and glacial acetic acid was added to adjust pH up to 11. Stirring was continued for 3 hours at a temperature of 100°C . After that, added 1 g of PDMA (10 wt.%) to the mixture and stirred again for 15 hours at room temperature. Then the reaction mixture was transferred into the autoclave and heated for 144 hours at a temperature of 150°C in the oven. The reaction product was be cooled, washed with aquademin, filtered, and dried at room temperature for one night. After that, the product was calcined for 8 hours at a temperature of 500°C . Synthesis of ZSM-5 from pro-analysis materials as references also was prepared with raw material from NaAlO_2 and TEOS. The as-synthesized crystals of mesoporous ZSM-5 were characterized by XRD instruments, FTIR, SEM, and pore size analyzer (BET).

Post-synthesis modification was carried out to obtain Co/ZSM5, test catalytic partial oxidation of methane to methanol in a vessel of stainless steel as a batch reactor, following the procedure have been reported previously [9] by mixing 0.2495 M cobalt solution (from $\text{Co}(\text{NO}_3)_2$) with the zeolite. After the impregnation process, the mixture was calcined at 500°C to obtain Co/ZSM-5.

2.4. Application for partial oxidation of methane to methanol

Test catalytic partial oxidation of methane to methanol in a vessel of stainless steel as a batch reactor, following the procedure have been reported previously [9]. The catalyst used for each reaction is 0.5 g, which has been activated at 500°C . The reaction was performed at 150°C with methane pressure of 0.75

bar and a nitrogen pressure of 2 bar with a variety of reaction time of 30 minutes and 60 minutes then extracted with ethanol, and characterized using Gas Chromatography-FID.

3. Results and discussion

3.1. X-Ray Diffraction (XRD)

Diffraction patterns of ZSM-5 from fly ash dan rice husk ash (nZSM-5) and ZSM-5 from pro-analysis materials (pZSM-5) showed the appearance of certain peaks at 7° to 9° and 22° to 25° 2 theta (figure 1), indicative of successfully synthesized ZSM-5 structure. Figure 1, also shows the peak intensity of nZSM-5 is lower than pZSM-5. It means that the crystallinity of pZSM-5 is higher than nZSM-5. Besides that, figure 1 also shows other pattern in position 2 theta 33° ; 36° ; 49° ; 57° , indicative of hematite and magnetite.

3.2. Fourier transform infra red (FTIR)

Figure 2 shows the FTIR spectra of nZSM-5 and pZSM-5. The characteristic absorption bands of ZSM-5 were found at around $1250\text{--}950\text{ cm}^{-1}$ ($\nu_{\text{asymetri T-O}}$), $1100\text{--}700\text{ cm}^{-1}$ ($\nu_{\text{simetri T-O}}$), and also were found at round $650\text{--}500\text{ cm}^{-1}$ indicated the presence of double 5 ring in ZSM-5 [10].

3.3. Thermal gravimetry analysis (TGA)

TG analyses of ZSM-5 were performed on nZSM-5 and pZSM-5. The TG curve (figure 3) of ZSM-5 particles shows weight loss up to three steps which is weight loss in the region $<150^\circ\text{C}$ showed a loss of water mass in the ZSM-5, while the area was around the $200\text{--}440^\circ\text{C}$ shows the decomposition and weight loss of PDDA. Then in the region $440\text{--}510^\circ\text{C}$ showed decomposition of TPAOH template.

3.4. Chemical content

Figure 4 shows the chemical content of nZSM-5 and pZSM-5 and the Si/Al ratio of pZSM-5 and nZSM-5 from are 16.73 and 20.10 respectively.

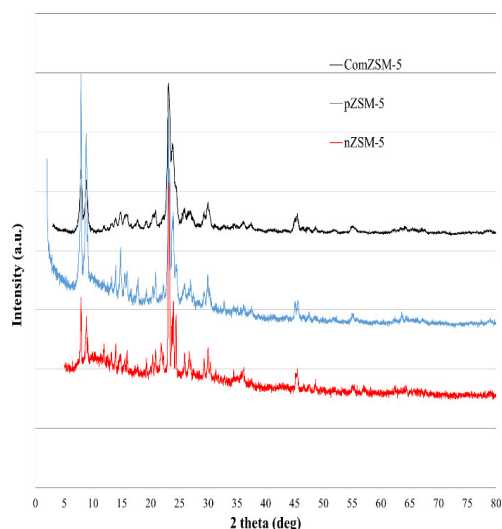


Figure 1. XRD Pattern of ZSM-5 synthesized (pZSM-5 and nZSM-5) and Com-ZSM-5.

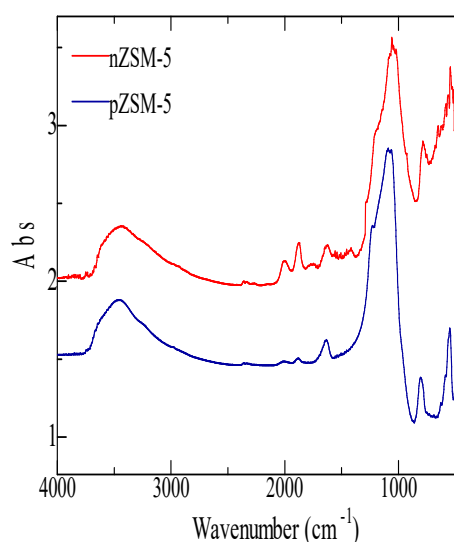


Figure 2. FTIR Spectra of ZSM-5 synthesized (pZSM-5 and nZSM-5).

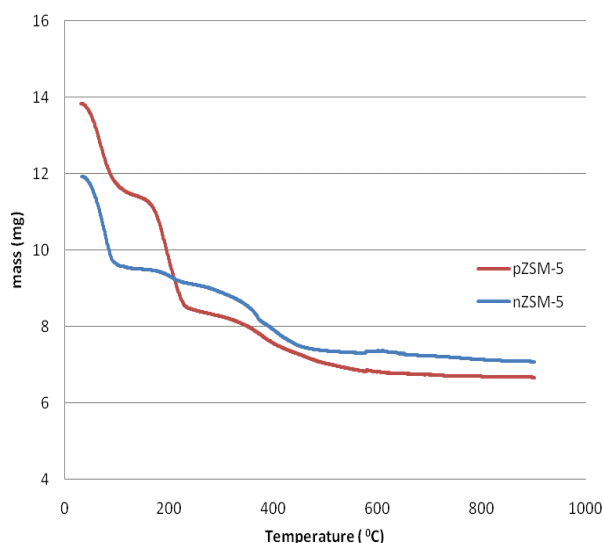


Figure 3. Thermogravimetry of as-synthesized ZSM-5.

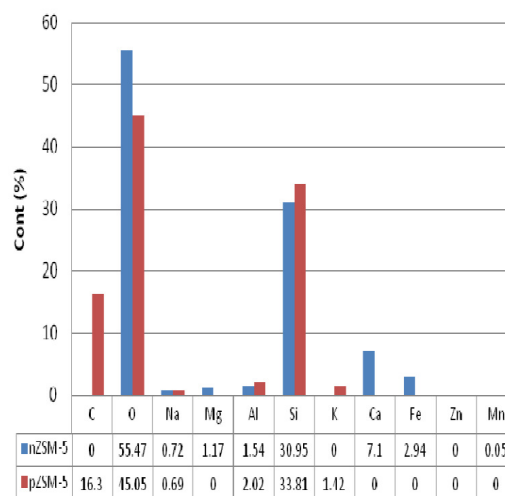


Figure 4. Analysis of chemical content of as-synthesized ZSM-5.

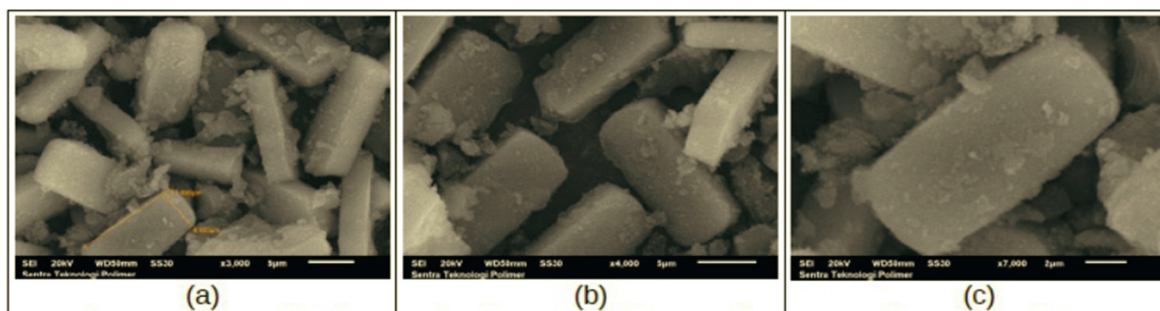


Figure 5a. The morphology of zeolite pZSM5 with magnification sequentially (a) 3.000 ×, (b) 4.000 ×, and (c) 7.000 ×.

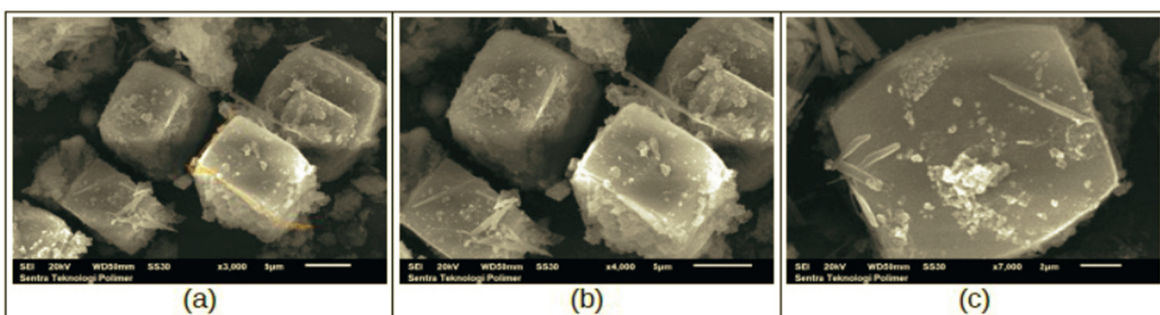


Figure 5b. The morphology of zeolite nZSM5 with magnification sequentially (a) 3.000 ×, (b) 4.000 ×, and (c) 7.000 ×.

3.5. Scanning electron microscopy (SEM)

The hexagonal morphology of nZSM5 and pZSM5 crystal were formed with unsmooth or rough surface, indicating the formation of mesoporous feature on the surface of the crystal (figure 5). SEM image also showed there were still many impurities in as-synthesized nZSM-5. Furthermore, the nZSM-5 has relatively shorter length compared to the pZSM-5.

3.6. Surface area analysis

The results of surface area analyses of nZSM-5 and pZSM-5 are summarized in table 1. It can be seen that the surface area of nZSM-5 from fly ash and rice husk ash is lower than the pZSM-5 from pro-analysis materials, due to ZSM-5 from fly ash and rice husk ash still has many impurities especially Fe which could act as inhibitor in zeolitization process. The pore volume of nZSM-5 is also lower than that of pZSM-5.

3.7. Catalytic test: partial oxidation of methane to methanol

Catalytic test on partial oxidation of methane to methanol in a vessel of stainless steel as a batch reactor, following the procedure have been reported previously [9]. The catalytic activity of Co/ZSM-5 also was tested. Prior to the catalytic reaction, the ZSM-5 catalyst must be first activated at a temperature of 500 °C with the aim to form cobalt oxide species which constitute the active site of the catalyst Co/ZSM-5. Furthermore, flushing was carried out using nitrogen gas to remove organic impurities, water vapour and excess oxygen in the reactor. The condition of the reaction was adapted from the work reported by Krisnandi *et al.* [9] and Bezniz *et al.* [11]. The first set of experiments was carried out at 150 °C with reaction time of 30 min and 60 min, and CH₄ pressure (P_{methane}) of 0.75 Bar in 200 cm³ stainless steel vessel. The results of this experiment are summarized in figure 6.

Figure 6 showed that hence the catalytic activity of ZSM-5 and Co/ZSM-5 from fly ash and rice husk was still inferior (7.08% and 12.43% conversion of methane) compared to the pro-analysis materials (28.33% and 37.65%) and commercial one (9.92% and 21.36%), they were potential to be used as catalysts in partial oxidation of methane to methanol. The activity of ZSM-5 and Co/ZSM-5 from fly ash and rice husk ash are inferior compared to the pro-analysis materials because ZSM-5 from fly

Table 1. Surface area analyses of ZSM-5 catalyst calculated from BET measurement.

Sample	S BET (m ² /g)	S ext (m ² /g)	V tot (cm ³ /g)	V meso (cm ³ /g)	V micro (cm ³ /g)	Average diameter pore (nm)
pZSM-5	294.75	104.44	0.594	0.495	0.099	8.11683
nZSM-5	43.759	43.759	0.287	0.287	-	26.2618

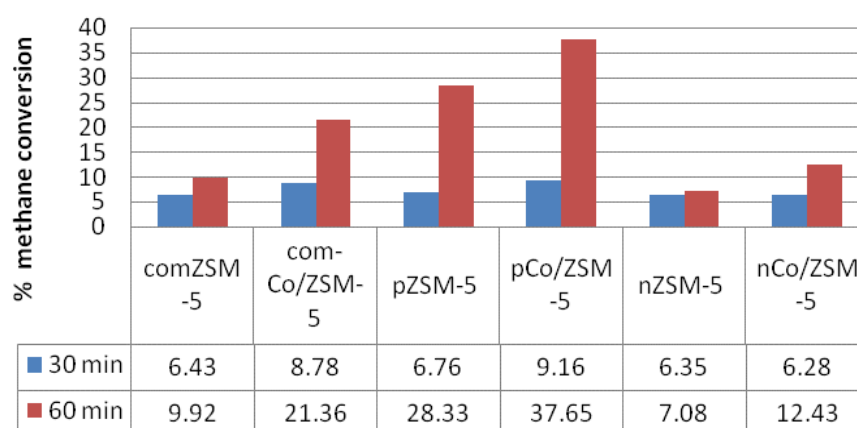


Figure 6. % methane conversion to methanol from reaction carried out at 150°C, t = 30 and 60 min and methane partial pressure of 0.75 bar.

ash and rice husk has lower surface area than ZSM-5 pro-analysis materials. The cobalt-loaded ZSM-5 catalysts gave higher conversion than the ZSM-5 without cobalt-loaded impregnated Co/ZSM-5, because it contains cobalt oxidic species at the zeolite outer surface, which becomes active sites that play important role in methane partial oxidation [11].

4. Conclusions

ZSM-5 zeolite catalysts from fly ash and rice husk have been prepared and their catalytic activities were tested in the partial oxidation of methane to methanol. The result showed that hence the catalytic activity of ZSM-5 and Co/ZSM-5 from fly ash and rice husk was still inferior (7.08% and 12.43% conversion of methane) compared to the pro-analysis sourced-counterpart (28.33% and 37.65%) and commercial one (9.92% and 21.36%), they were potential to be used as catalyst in the partial oxidation of methane to methanol.

Acknowledgments

This research was funded by Hibah PUPT BOPTN No. 0545/UN2.R12/HKP/05.00/2015 and BPPT SK No. No.211a/2014.

References

- [1] Bukhari S S, Behin J, Kazemian H and Rohani S 2015 *Fuel* **140** 250-266
- [2] Kouprianov V I 2002 *Fuel Process. Technol.* **76** 187-9
- [3] Zacco A, Borgese L, Gianoncelli A, Struis R P W J, Depero L E and Bontempi E 2014 *Environmental Chem Lett.* **12** 153-75
- [4] Zhao X S, Lu G Q and Zhu H Y 1997 *J. Porous Mater.* **4** 245-51
- [5] Chareonpanich M, Namto T, Kongkachuichay P and Limtrakul J 2004 *Fuel Processing* **85** 1623-34
- [6] Groen J C, Moulijn J A and Perz-Ramirez J 2005 *Microporous and Mesoporous Materials* **87** 153-61
- [7] Panpa W and Jinawath S 2009 *Applied Catalyst B: Environmental* **90** 389-94
- [8] Mohamed M M, Zidan F I and Thabet M 2008 *Microporous and Mesoporous Materials* **108** 193-203
- [9] Krisnandi Y, Putra Bimo A P, Bahtiar M, Zahara, Abdullah M and Howe R F 2015 *Procedia Chemistry* **14** 508-15
- [10] Naskar M K, Kundu D and Chatterjee M 2012 *J. American Ceramic Society* **95** 925-30
- [11] Beznis N V, Weckhuysen B M and Bitter J H 2010 *Catalysis Lett.* **136** 52-6