IJFAC

Indonesian Journal of
Fundamental and Applied Chemistry

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Synthesis, Characterization of ZSM-5 Catalyst for Catalytic Pyrolysis of Empty Fruit Bunches

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Abstract

ZSM-5 is known as a heterogeneous catalyst in the process of petroleum cracking. Zeolite has narrow pores so it needs synthesis to form mesopore so that reactant molecules can enter the active site in ZSM-5 mesopore. In this study, mesopore formation was carried out by adding Si/Al components with a ratio of 20 derived from tetraethyl orthosilicate, aluminum isopropoxide and TPAOH template with hydrothermal process. The resulting ZSM-5 was characterized using x-ray diffraction, scanning and electron microscopy (SEM). The XRD characterization results showed that the ZSM-5 synthesized to form mesopore was seen from a fairly high peak intensity in the range at 2-theta were 8.11, 9.01°; 23.27°; 23.49°; and 24.13°. The results of this study already have the same structure as the commercial ZSM-5. Characterization of SEM-EDS showed that Si-Al and Na elements in ZSM-5 were 96.43%, 3.56% and 0% wt, respectively. With a magnification of 20000x, this cluster is quite homogeneous even though the crystallization formed is not well aggregated. This ZSM-5 catalyst will be applied to the process of biomass into bio-oil.

Keywords: ZSM-5 catalyst, zeolite, hydrotermal treatment, tetraethyl orthosilicate

Abstrak (Indonesian)

ZSM-5 dikenal sebagai katalis heterogen dalam proses perengkahan minyak bumi. Zeolit memiliki pori-pori yang sempit sehingga perlu sintesa untuk membentuk mesopore agar molekul reaktan dapat masuk ke site aktif pada mesopore ZSM-5. Pada penelitian ini, pembentukan mesopore tersebut dilakukan dengan menambahkan komponen Si/Al dengan ratio 20 yang berasal dari tetraethyl orthosilikat, alumunium isopropoxide dan template TPAOH dengan proses *hydrotermal*. ZSM-5 yang dihasilkan dikarakterisasi menggunakan *x-ray diffraction, scanning* dan *electron microscopy (SEM).* Hasil karakterisasi XRD menunjukkan bahwa ZSM-5 yang dihasilkan membentuk mesopore terlihat dari intensitas puncak yang cukup tinggi berada pada kisaran di 2-theta yaitu 8.11°, 9.01°, 23.27°, 23.49° dan 24.13°. Hasil penelitian ini sudah memiliki struktur yang sama dengan ZSM-5 komersial. Karakterisasi SEM-EDS menunjukan elemen Si-Al dan Na dalam ZSM-5 adalah 96,43-3,56% dan 0% wt. Perbesaran 20000x menunjukkan *cluster* ini cukup homogen walaupun kristalisasi yang terbentuk tidak ter-agregasi dengan baik. Katalis ZSM-5 ini akan diaplikasikan pada proses konversi pirolisis biomassa menjadi *bio-oil.*

Kata Kunci: katalis ZSM-5, zeolit, hydrotermal treatment, tetraethyl orthosilicate

Article Info

Received 15 January 2019
Received in revised 1 March 2019
Accepted 7 March 2019
Available online 10 June 2019

INTRODUCTION

Pyrolysis is a thermal decomposition reaction of polymeric materials at intermediate temperatures between 400 °C and 600 °C below the atmosphere in a non-oxygen state, and this process is considered to be one of the most suitable method for producing

bio-oil with high yield and quality from biomass [1]. Bio-oil produced through the pyrolysis process has great potential to replace petroleum-based liquid fuel as a cleaner product that is sustainable because of the neutrality of carbon dioxide (CO_2) from biomass. The process that has been carried out by many researchers to produce bio-fuel includes thermal cracking that takes place at high temperatures and pressures, causing large energy requirements, so currently cracking processes are being developed using heterogeneous catalysts to reduce the need for high reaction temperatures [2].

The heterogeneous catalyst support that is widely used in the catalytic cracking process is zeolite [3]. Zeolite is the best catalyst for cracking because it has high thermal stability, has a microcrystalline structure and pores that should be able to accommodate reactant molecules in order to react within the active site of the catalyst [4].

ZSM-5 is a zeolite which is often used as a catalyst in petroleum refining. ZSM-5 has intersecting pore network consisting of straight channel and zig-zag channels in nanoporous form. Nanocrystalline ZSM-5 shows an increase in selectivity and toluene conversion to cresol and a decrease in coke formation relative to conventional ZSM-5 materials [5].

In general, ZSM-5 catalysts are synthesized using commercial chemicals as a source of silica and alumina. Tetraethylorthosilicates (TEOS) is the most widely used chemical as a source of silica [6-9] and the organic template used in the synthesis of ZSM-5 catalysts as the directing agents of the MFI structure that is widely used is tetrapropylammonium bromide, TPABr [10-13] or tetrapropylammonium hydroxide, TPAOH [14-16].

The synthesis process of ZSM-5 catalyst in this study was carried out based on the method referred by Nazarudin [17]. To produce a ZSM-5 catalyst, the ratio of the use of Si/Al component sources was 20. Determination of the ratio was based on the results of Nazarudin [17] and the calcination temperature of ZSM-5 crystals was modified in this study. In Song et al's study [18], synthesized ZSM-5 crystals were then calcined at the temperature of 600 °C for 5 hours consisting of agglomerated particles and forming aggregations indicated by the results of characterization with SEM. Dao-ke et al. [19] in his study produced a HZSM-5 catalyst, which prior tothe ion-exchanging process between Na-ZSM-5 and NH_4NO_3 for the formation of HZSM-5, Na-ZSM-5 Zeolite was calcined at the temperature of 550 °C.

Commercial ZSM-5 is used for the comparison of the synthesized ZSM-5 catalyst properties. Then, the resulting catalyst was analyzed using SEM and XRD to understand its characteristics

MATERIALS AND METHODS

Materials

The materials used for the synthesis of ZSM-5 include tetraethylorthosilicates ($Si[OET]_4$), tetrapropylammonium hydroxide (TPAOH), aluminum isopropoxide $Al[OPr]_3$, NaOH and Aquadest.

Methods

ZSM-5 catalyst with SiO_2/Al_2O_3 = 20 ratio was synthesized using the Nazarudin [17] method, Si $[OET]_4$, TPAOH, Al $[OPr]_3$, *Aquadest* and NaOH methods with mass ratio 45: 22: 1: 30: 0.03 is mixed and stirred at room temperature 30 °C for 24 hours until clear solution is formed. Clear solution of ZSM-5 mixture that has been formed is put into a reactor with Teflon material for hydrothermal treatment at 165 °C for 5 days. ZSM-5 crystals are formed, washed and centrifuged with distilled water to dissolve contained impurities with the help of a vacuum pump so that the impurities separate from the liquid to the pH of the water and the impurity reaches a neutral pH = 7. Followed by drying at temperature 105 °C for 24 hours. ZSM-5 crystals are calcined at 550 °C for 5 hours to remove the TPAOH template.

Catalyst Characterization

The ZSM-5 catalyst crystals that formed were analyzed by SEM (Scanning Electron Microscopy) method with tool type (SEM-EDX) ZEISS EVO® MA 10 from the University of Lampung UPTLTSIT laboratory.

The crystal structure and relative crystallinity of zeolite are determined by X-ray diffraction (XRD). The characterization was performed by XRD produced by Phillip with the initial position of 2 theta is 5.0084 and the final position 59.9864 with continuous scan type specimen extension data 10.00 mm and measurement temperature of -273.15 °C with Cu as anodized material and Diffractometer type was XPert MPD.

RESULTS AND DISCUSSION

The catalyst produced in this study was obtained from the results of synthesis using references from Nazarudin method [17]. After all synthesis materials were mixed and stirred for 24 hours then clear solution was formed. Clear solution that produced was crystallized in a closed hydrothermal system at

high temperature.

This hydrothermal process involves water and heat, where the mixture is heated at a relatively high temperature in a closed autoclave so that there is a equilibrium between water vapor and solution. The closed autoclave makes water vapor will not run out, so none part of the solution is lost. In the hydrothermal process, a condensation reaction occurs which allows the formation of new bonds Si, Al-O-Si, Al (T-O-T) [20].

ZSM-5 becomes a crystal at temperatures above 100 °C by adding organic bases such as tetrapropylammonium (TPAOH) [21].The resulting ZSM-5 catalyst has a white form like powder.(Figure 1)

Figure 1. Synthesized ZSM-5 catalyst

Characterization of ZSM-5 catalysts with XRD

XRD analysis is performed to identify and determine quantitatively the crystal phase form of ZSM-5. The result of XRD analysis is a difractogram which shows the crystallinity level of a solid in the form of the sharpness of specific peaks. The data that obtained from XRD are diffracted X-ray diffraction intensities and 2θ angles.

The ZSM-5 XRD pattern formed a peak on the diffractogram at 2-theta (Figure 2), were 8.11°, 9.01°, 23.27°, 23.49° and 24.13°.

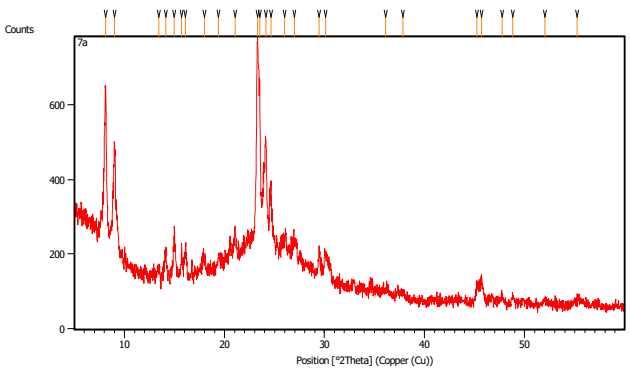

Figure 2. XRD ZSM-5 diffractogram

The ZSM-5 diffraction peaks (Figure 2) showed a similar pattern to ZSM-5 difactogram standard (Figure 3), were at 2-tetha 7-9° and at 23.05° and 23.8°. The resulting pattern also shows identical characteristic peaks of ZSM-5 that have been synthesized in the literature [15,18].

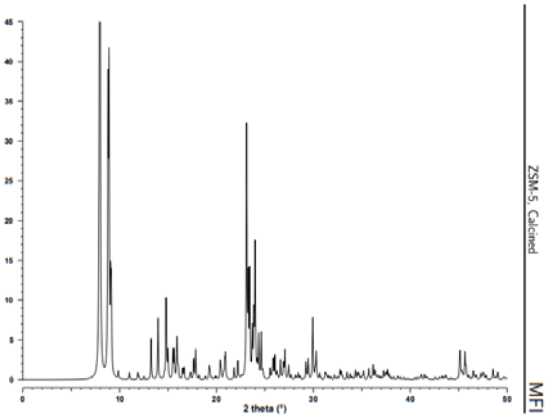

Figure 3. ZSM-5 Difractogram Standard [23]

The ZSM-5 MFI structure in Figure 3 is a ZSM-5 diffractogram standard used to compare the crystallinity level in the form of sharpness of the peaks of a solid ZSM-5 synthesized with a standard ZSM-5.

The peak at θ around 7-8° and around 23-25° indicates that the ZSM-5 has been formed [22]. It can be concluded that the synthesis catalyst is included in the type of MFI structure. This MFI structure is obtained from the use of TPA^+ as a template. The X-ray diffraction pattern in Figure 1 shows that the synthesized catalyst consists of MFI phase with high crystallinity and there is no other crystalline phase in the synthesis results of this ZSM-5 and has the same structure as the commercial ZSM-5. Crystallization of the synthesis results of this ZSM-5 is quite good because the ZSM-5 diffractogram shows sharp peaks and good peak separation.

Characterization of ZSM-5 catalyst by SEM-EDS

Characterization using SEM aims to determine the zeolite morphology, both the surface, the shape of the crystal that has been produced. Whereas EDS (Dispersive X-Ray Spectroscopy) is a form of elemental analysis to determine the levels of the elements contained in zeolites, such as Si, Al, Na and their balance cations. In order for this surface morphology to be revealed more clearly, the analysis is done with 2x magnification, namely 10000x and 20000x. Based on existing references, the ZSM-5 has a hexagonal crystal morphology. The analysis results with a magnification of 10000x (Figure 4A) indicate that the particles of ZSM-5 are not forming the groups (clusters) with polymorphous (not homogeneous) structures. The analysis results with a

magnification of 20000x (Figure 4B) show that this cluster is quite homogeneous even though the crytallization formed is not well aggregated.

In the results of the study Song et al [18], the particles of ZSM-5 were forming the clusters and there was an aggregation process between ZSM-5 particles.

However, with the diffactogram of the ZSM-5 XRD analysis (Figure 2) showing a similar pattern to the standard ZSM-5 diffractogram, then it can be confirmed that the synthesized ZSM-5 has the same structure with the commercial ZSM-5.

EDS analysis on the synthesis results of ZSM-5 was carried out to determine the elemental composition in the sample. The results of the EDS analysis are presented in Figure 5. Based on the results of EDS analysis, it is known that the microstructure of the synthesized samples of ZSM-5 contains compositions of elements Si, Al, and Na with a relative mass percentage of 96.43%, 3.57% and 0%, respectively.

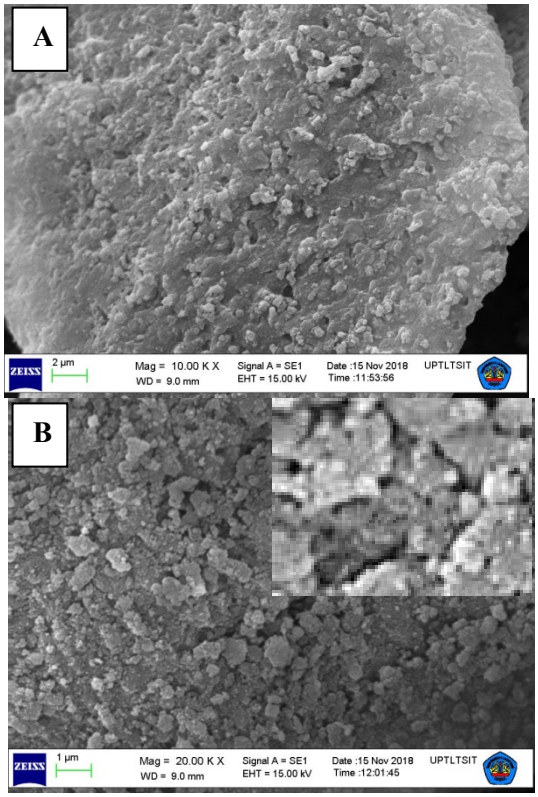

Figure 4. ZSM-5 (A) catalyst microstructure with magnification10000x and (B) magnification of 20000x

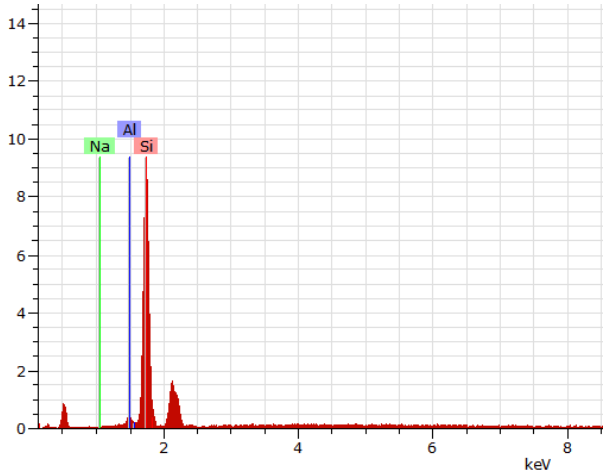

Figure 5. EDS spectrum and composition of synthesized ZSM-5 catalysts

CONCLUSION

ZSM-5 is synthesized with Si / Al 20 ratio with a hydrothermal process. The XRD characterization results showed that the ZSM-5 produced to form mesopore was seen from a fairly high peak intensity in the range at 2 theta namely 8.11°, 9.01°, 23.27°, 23.49° and 24.13°. The results of this study already have the same structure as the commercial ZSM-5. The characterization of SEM with a magnification of 20000x on micrographs showed that the particles of ZSM-5 formed a fairly homogeneous cluster but the crystallization formed was not well aggregated and the SEM-EDS characterization showed that Si-Al and Na elements in ZSM-5 were 96.43%, 3.56% and 0% wt.

ACKNOWLEDGEMENT

The authors are thankful to Energy and Nano Material Centre, LPPM, University of Jambi for providing the materials and tools necessary for this research.

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