Synthesis and characterization of ZSM-5 zeolite with micro- and hierarchical pore structures from Bayat natural zeolite

Synthesis and characterization of ZSM-5 zeolite with micro- and hierarchical pore structures from Bayat natural zeolite

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Abstract. Synthesis of ZSM-5 (Zeolite Socony Mobil–5) has been carried out using Bayat natural zeolite as silica and alumina source. Pretreatment on Bayat natural zeolite was performed through the process of activation, purification, dealumination, and fragmentation. The purpose of activation process is to remove the polar impurities, free oxide in the surface that cover up the pores and release the water that trapped in the pores of the crystals. The purification was conducted using Na-acetate buffer solution with ratio 1:3 (w/v). The dealumination process with 2M HCl was carried out to increase the Si/Al ratio. Fragmentation process then was carried out by using NaOH as much as 50% of NaOH was mixed with Bayat natural zeolite. Synthesis of ZSM-5 was performed using single templates method by adding TPAOH (Tetrapropylammonium hydroxide) as micropore structure directing agent. Furthermore, synthesis of hierarchical ZSM-5 using double templates method was also carried out in which PDDAM (Poly(acrylamide-co-diallyldimethylammonium chloride)) as mesoporous directing agent. The results showed XRD pattern of Microporous ZSM-5 and Hierarchical ZSM-5 had specific peaks at position 2 theta position of 7-10˚ and 22-25˚ which are the characteristics of ZSM-5 zeolite. The Si/Al molar ratio of microporous ZSM-5 and hierarchical ZSM-5 are 32.34 and 43.53.

Keywords: Bayat natural zeolite, ZSM-5 microporous, ZSM-5 hierarchical, TPAOH, PDDAM

1. Introduction

Indonesia is a country that has many volcanoes that potentially produce natural zeolite from volcanic dust. Zeolite is an aluminosilicate material with three-dimensional frameworks that consists of SiO_4 and AlO_4 tetrahedral arranged regularly, in which each oxygen atom is shared between two tetrahedral. The replacement of Si^{4+} with Al^{3+} in tetrahedral structure creates negative formal charge and counterbalanced by exchangeable cations [1]. But in the natural zeolite there are some impurities, therefore it is necessary to conduct pretreatment of natural zeolite to remove the impurities [2].

ZSM-5 (Zeolite Socony Mobil-5), which was developed in 1972, is usually synthesized using hydrothermal method from a liquid of alkaline silicate aluminate using tetrapropyl ammonium hydroxide (TPAOH) as a microporous template. ZSM-5 is one of the best working heterogeneous catalysts at industry especially in coal, oil and natural gas industries [3].

This research is focused on synthesis microporous and hierarchical ZSM-5 by using silica and alumina source from Bayat natural zeolite [4]. Before synthesis of zeolite, natural zeolite was

subjected to pretreatment, such as zeolite activation process, purification, dealumination and fragmentation. The synthesis of hierarchical ZSM-5 was carried out using double template method accompanied by addition to TPAOH as micropore directing agent and PDDAM (Poly(acrylamide-co-diallyldimethylammonium chloride)) as mesoporous directing agent [5]. As comparison microporous ZSM-5 was also synthesized, without addition of PPDA.

2. Experimental

2.1. Materials.

Bayat natural zeolite, deionized water, hydrochloric acid (HCl), solid sodium hydroxide (NaOH), glacial acetic acid (CH_3COOH), Na-citrate-bicarbonate solution, Na-acetate buffer ($C_2H_3NaO_2$), 30% H_2O_2 solution, Liquid Silica (Ludox 40%), solid sodium ditionate ($Na_2S_2O_4$), Tetrapropyl ammonium hydroxide (TPAOH) 1M and Poly(acrylamide-co-diallyldimethylammonium chloride (PDDAM).

2.2. Pretreatment of natural zeolite Bayat.

Pretreatment of natural zeolite bayat was performed through the process of activation, purification, dealumination, and fragmentation. Activation of zeolite was carried out by immersing the zeolite in distilled water with a ratio of 1:3 (w/v), and then purification was conducted using Na-acetate buffer solution with ratio 1:3 (w/v). In the dealumination process, the purified zeolite was added with 2M HCl and then stirred at 100 °C under reflux condition for 2 hours. Natural zeolite fragmentation was done through submolten salt technique system (SMS) [6] using a NaOH pellets with molar ratio of 2:1 (w/w) in deionized water. Characterizations of natural zeolite were conducted with Energy Dispersion X-Ray (EDX), X-Ray Diffraction (XRD) and Fourier-transform Infrared (FTIR) instruments.

2.3. Synthesis of ZSM-5 zeolites.

A mixture of fragmented Bayat natural zeolite, deionized water, TPAOH 1M with molar ratio of 64.34 SiO_2:1 Al_2O_3:10.08 $(TPA)_2O$:3571.67 H_2O, with addition of Ludox 40% (to reach the desired amount of Si) [2] was prepared under vigorous stirring at 100°C for 3 hours. Then, in order to control the pH of the mixture to be 11 ± 0.2, glacial acetic acid was added to the mixture. Stirring was carried out further for 3 hours at 100°C and at room temperature for 24 hours. Afterward, the mixture was transferred into an autoclave made from stainless steel with a teflon-lined inside for crystallization at 150 °C for 144 hours. After filtration, the white solid product was washed with the deionized water and dried at 60°C for 12 h and 105°C for 1 hour. Then, microporous ZSM-5 was calcined at 550°C for 8 hours and characterized using XRD, FTIR, EDX, BET and instruments. Similar procedure was employed in synthesis of hierarchical ZSM-5 zeolite, in which poly dimethyl dialyl ammonium chloride acrylamide (PDDAM) was added at room temperature, as a secondary template, continued with stirring for 24 hours, before transferred into the autoclave for further heated at 150 °C for 144 hours.

3. Results and discussion

3.1. Pretreatment of Bayat natural zeolite characterization

Before synthesis of ZSM-5 from Bayat natural zeolite, it was necessary that the natural zeolite to undergo pretreatment process, in order to remove impurities and to breakdown the structure of the zeolite framework, forming SiO_4^{4-} and AlO_4^{5-} active [1,4,6,7]. The result of FTIR (figure 1) showed typical spectra of aluminasilica compound, i.e. the peaks in the area of wave number 1250-1050 cm^{-1} and 1100-700 cm^{-1} assigned for the stretching vibration for SiO/AlO asymmetric and symmetric, respectively [8]. In the activation process, the zeolite can absorb a lot of water as indicated by the increased intensity of the H-OH bending vibration of water molecules at 1620 cm^{-1}.

There is a new peak assigned for stretching vibration of Si-O$^-$ Na^+ Al-O$^-$ Na^+ at 1461 cm^{-1} appeared in fragmented zeolite. Furthermore, in the region between 500-650 cm^{-1} and 1500-1700 cm^{-1}, peaks for finger print of zeolite framework and H-OH bending vibration disappeared in fragmented zeolite. It

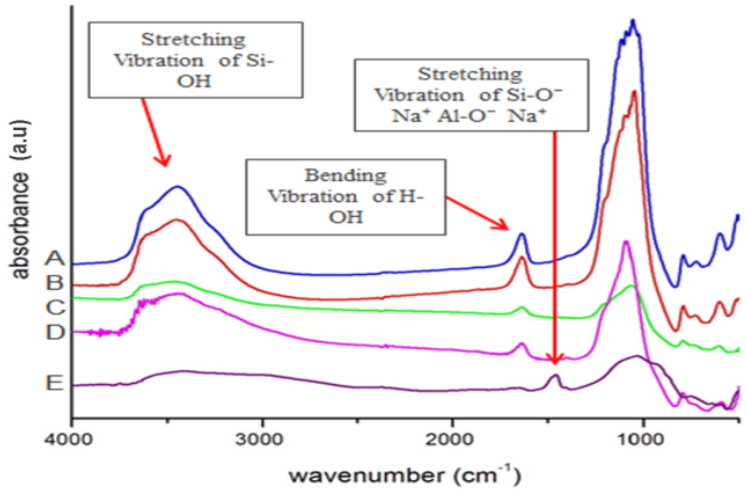

Figure 1. FTIR spectra of (a) raw, (b) activated, (c) purified, (d) dealuminated, (e) fragmented Bayat natural zeolite

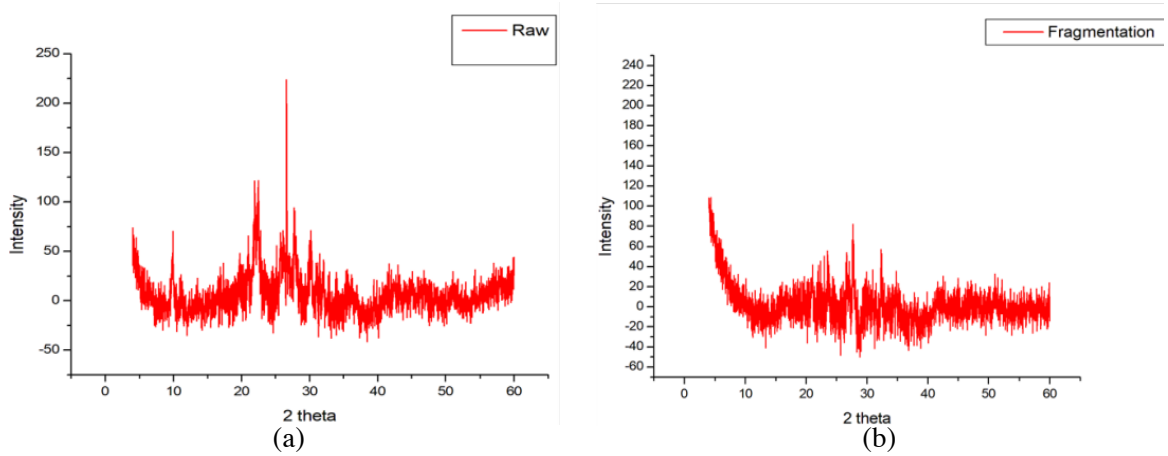

Figure 2. Pattern of XRD (a) raw zeolite and (b) fragmented zeolite

indicates that the zeolite framework has been destructed [4]. This is supported by the XRD results in figure 2. Bayat raw zeolite diffraction pattern shown in figure 2a shows typical pattern of Mordenite structure with peaks at 2θ of 9.85°; 22.21°; and 25.61°. After fragmentation process, those peaks disappeared, indicative of the successful fragmentation process in which the zeolite structure was destroyed to become more amorphous material.

3.2. Zeolites ZSM-5 characterization

Si and Al active rearranged to form ZSM-5 zeolite framework by synthesis process. In the synthesis of ZSM-5, the purpose to use organic templates is to direct the shape and size of the pores in the structure [5]. In the synthesis of microporous ZSM-5 using single template, TPAOH was added to direct the development of micro-pores. Meanwhile, for the synthesis of hierarchical ZSM-5, using double template, PDDAM was also added to develop mesostructure. The existence of templates can be seen with the FTIR spectra (figure 3). From the results of both as-synthesis ZSM-5 zeolites, before calcination (figure 3a and figure 3b), the spectra contain peaks at 1470-1350 cm^{-1}, which is a absorption band of C-H bending vibration, and at 2960-2850 cm^{-1} which is an absorption band of C-H stretching vibration. After calcination, those peaks disappeared from the FTIR spectrum (figure 3c and

Table 1. EDX analysis of zeolite materials (% molar)

Elements	Raw	Fragmentation	Microporous ZSM-5	Hierarchical ZSM-5
Na	0.02	1.07	0.02	0.01
Al	0.24	0.10	0.06	0.04
Si	1.28	0.89	2.06	1.84
Ratio Si/Al	5.33	8.9	32.34	43.53

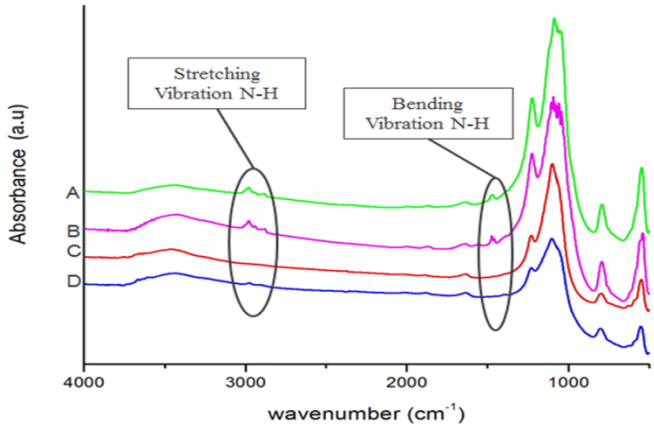

Figure 3. FTIR spectra of synthesized (a) microporous ZSM-5 and (b) hierarchical ZSM-5 before calcination; (c) microporous ZSM-5 and (d) hierarchical ZSM-5 after calcination.

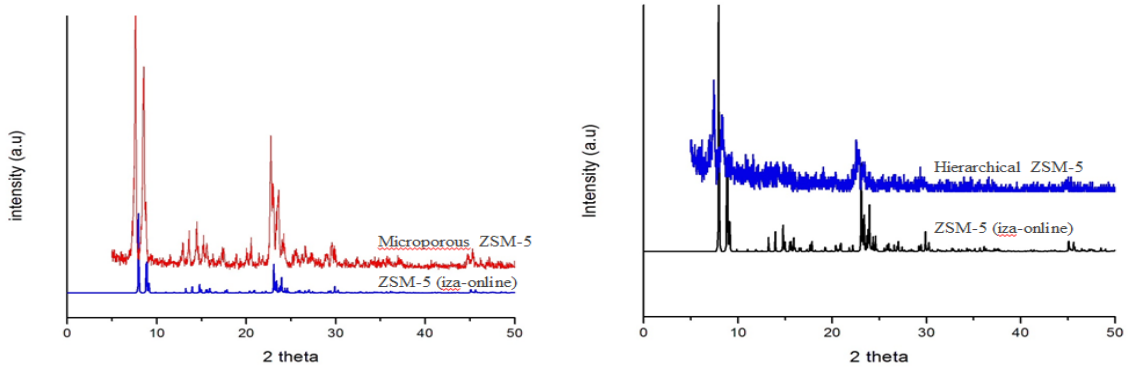

Figure 4. Pattern of XRD for (a) microporous ZSM-5 and (b) hierarchical ZSM-5, both simulated from IZA online database and synthesized from Bayat natural zeolite

figure 3d). This indicates that the calcination process successfully removed organic templates, and zeolites become porous because there are empty space, which previously occupied by the template.

The result of EDX analysis (table 1) showed the raw Bayat natural zeolite has low Si/Al ratio of 5.33 and for the fragmentation ZAB of 8.9. The process of pretreatment is successful because there is an increase of Si/Al ratio in natural zeolite. After synthesis, ratio of Si/Al increase again, and it can be seen that the Si/Al molar ratio of hierarchical ZSM-5 (43.53) is higher than that of microporous ZSM-5 (32.4).

XRD result showed ZSM-5 sythesized has typical peaks at 2θ position of 7-10° and 22-25° [9]. Figure 4a and figure 4b showed the simulated pattern of ZSM-5 from IZA online database structure [10] and the patterns of ZSM-5 synthesized from Bayat natural zeolite. In general, they have similar specific diffraction patterns, suggesting that ZSM-5 has been successfully synthesized.

4. Conclusions

Synthesis of ZSM-5 zeolite with microporous and hierarchical structures using Bayat natural zeolite as silica and alumina source and addition of LUDOX is successful. This is evidenced by the XRD results addressing some typical zeolite ZSM-5 peaks. The Si/Al molar ratio of microporous ZSM-5 and hierarchical ZSM-5 are 32.34 and 43.53. Characterization by FTIR show that modification using ion-exchange method aims to produce zeolites that have high activity indicated has been successful.

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