Synthesis and Characterization of ZSM-5 Zeolite from Dealuminated and Fragmentated Bayat-Klaten Natural Zeolite

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Abstract. Synthesis of ZSM-5 zeolite was conducted using natural zeolite of Bayat-Klaten by employing fragmentation method of sub-molten system through breaking zeolite framework into its monomer in alkaline condition at 250°C. Prior to fragmentation, one part of zeolite was treated with dealumination and the other one without dealumination, labeled as ZSM-5_a and ZSM-5_wa, respectively. Characterization with FTIR, XRD, and EDX showed that the fragmentation was successful, in which the structure of zeolite was damaged and the infrared bands due to AlO_4 and SiO_4 were appeared. The synthesis of ZSM-5 was performed hydrothermally using tetrapropylammonium hydroxide (TPAOH) as a directing agent of pore structure and addition of LUDOX (40% silica suspension in water). The XRD characterization showed the as synthesized materials had the structure of ZSM-5 zeolites with high crystallinity. Imaging with SEM showed the characteristic of hexagonal ZSM-5 crystals. The BET surface area analysis showed a typical surface area of microporous zeolite, 262 m^2/g, and pore diameter of 1.496 nm; indicating that the ZSM-5 zeolite obtained was micropore size. The Si/Al ratio of ZSM-5_a and ZSM-5_wa were 18 and 21, respectively. These results indicated that Bayat-Klaten natural zeolite can be used as silica and alumina source for high crystalline ZSM-5 with medium Si/Al ratio and having good thermal stability. Thus, these materials are potential to be tested as fluid hydrocracking catalyst.

Keywords: dealumination, fragmentation, ZSM-5, Bayat-Klaten natural zeolite

1. Introduction

Indonesia has large potential of natural zeolite production, such as that located in Lampung, West Java, Central Java, East Java, East Nusa Tenggara, and Sulawesi. Zeolites are aluminosilicate material with a three-dimensional framework consisting of SiO_4 tetrahedral and AlO_4 arranged regularly where every oxygen atom is shared between two tetrahedral. The structure of the zeolite framework and make the zeolite has many uses, unique properties, and easy to modify, so that the rapidly growing research on zeolites. However, the natural zeolite has some disadvantages, including having a low purity because it contains a lot of impurities and poor crystallinity. Therefore, its utilization becomes less optimal compared with synthetic zeolite [1].

The large of potential resource of natural zeolite in Indonesia affected this natural zeolite is cheaper than synthetic one. Based on the acidity properties of the natural zeolite and the ability to catalyze of synthetic zeolite, we need some process and modification of natural zeolite in order to compete with synthetic zeolites [2]. To improve the utilization of natural zeolite, silica and alumina contents presented
in the natural zeolite can be used as a source of Si and Al source to form a zeolite with a high purity level. Acid treatment to zeolite should be conducted in order to eliminate Al and cause deformation on its structure. Furthermore, depolymerization of zeolite structure through sub-molten technique was required to obtain aluminite and silicate fractions. The defective zeolite mixture was then used as the Si and Al source for ZSM-5 zeolite synthesis.

2. Materials and methods

2.1. General

Natural zeolite was obtained from Bayat, Central Java, Indonesia. The chemicals used were hydrochloric acid (HCl) p.a., sodium hydroxide (NaOH) pellet, acetic acid glacial (CH₃COOH) p.a., hydrogen peroxide (H₂O₂) 30% p.a., tetrapropylammonium hydroxide (TPAOH) 1M, colloidal silica (LUDOX 40%), and tetraethylorthosilica (TEOS) from Sigma Aldrich, sodium ditionate (Na₂S₃O₇), sodium-citrate-bicarbonate, and sodium-acetate buffer (NaOAc) from Merck.

2.2. Pretreatment of Natural Zeolite

Modification of Bayat natural zeolite consisted of physical activation, purification, dealumination, and fragmentation. Natural zeolite was crushed using a grinder and filtered with a sieve. Activation of natural zeolite was performed by washing the zeolite with deionized water (1:3 w/v) under stirring for 3 h. The solid phase was then dried at 300°C for 1 h. The purification process was conducted following Ming and Dixon, 1987 [3]. The activated natural zeolite was treated with 1 M NaOAc buffered to pH 5, 30% H₂O₂, and dithionite-citrate-bicarbonate. After purification, dealumination process was conducted by stirring zeolite in 1 M HCl solution (10 g zeolite/100 mL solution) at 100°C for 2 h under reflux. The solid phase was washed with demineralized water and dried at 65°C. Pretreated zeolite, with or without acid treatment, was fragmented using sub-molten salt system (SMS) technique, by mixing it with strong base (NaOH pellet), and ratio of zeolite:NaOH was 2:1. Incipient amount of water was poured into the mixture and then heated at 250°C with stirring.

2.3. Synthesis of ZSM-5 Zeolite

The fragmented zeolite (with or without acid treatment) was added to deionized water contained 1 M TPAOH and stirred using a magnetic stirrer at 100°C. LUDOX 40% and TEOS were also added to the mixture until the composition of molar ratio in the mixture was 64.35 SiO₂: 1 Al₂O₃: 10.08 TPAOH: 6 Na₂O: 3571.67 H₂O [4]. CH₃COOH was added to regulate the pH of the mixture (pH 11 ± 0.2). Stirring was done for 3 to 24 h. The gel formed then was transferred into the autoclave to be further heated at 150°C for 144 h. The resulting product was collected by filtration and washed with aquades, then dried at 60°C for 12 h, and 105°C for 1 h. Furthermore, calcination was done at 550°C for 8 h to remove the templates. The ZSM-5 synthesized from zeolite that undergo acid treatment before fragmentation was labeled ZSM-5_wa. While the counterpart that was synthesized using fragmented zeolite without acid treatment was named ZSM-5_za.

2.4. Characterization of zeolites

Characterization of natural zeolite and ZSM-5 were done using XRD, FTIR, and SEM-EDX. BET was also conducted for characterization of ZSM-5.

3. Results and discussion

Characterization using XRD was conducted to find out the crystallinity and typical peak pattern of the Bayat natural zeolite. Bayat raw zeolite diffraction pattern (Figure 1A) indicated peaks at 2θ of 9.85°, 22.21°, and 25.61°. The resulting peak did not have a sharp intensity, since the crystallinity contained in Bayat zeolite was still low or amorphous. Furthermore, these peaks were similar to the typical peak of the mordenite type zeolite (JCPDS Card No.29-1257) main peak of 9.77°, 22.20°, and 25.63°.
From the diffraction pattern (Figure 1B(a-c)) of the Bayat natural raw zeolite showed the same pattern with the pattern of active zeolite diffraction and purification. This diffraction pattern indicated that the activation and purification process of Bayat natural zeolite did not alter its crystal structure. Figure 1B(d-e) showed that peaks appeared at 2θ of 20.90°, 26.68°, and 36.57° were the peak for quartz (Quartz). This is because the fragmentation process aims to destroy the zeolite frame structure, breaking the Si-O-Si and Si-O-Al bonds into Si-O and Al-O active, therefore the tetrahedral structures of Si-O and Al-O will be damaged and their structural shape is no longer intact [5].

**Figure 1.** XRD patterns of Bayat natural zeolite A. raw and simulated mordenite in IZA-online, B. (a) raw, after pretreatment: (b) purification and (c) activation, and after fragmentation: (d) acidic and (e) without acidic treatment

Figure 2 showed the FTIR spectra of as-synthesized ZSM-5 before and after calcination. ZSM-5 FTIR spectra before calcination showed peaks at 2960-2850 cm\(^{-1}\) belongs to vibration band of C-H and 1470-1350 cm\(^{-1}\) belongs to C-H bend vibration. This absorption band came from a template used in the process of zeolite synthesis, TPAOH. The calcination process was performed to remove the organic template used in the synthesis. With the loss of this template, the pores and channels on the zeolite become empty. The loss of template in ZSM-5 after calcination was showed by the loss of the vibration band C-H vibration absorption and C-H bending vibration [6]. With the calcination process, the absorbing bands at 3600 cm\(^{-1}\) was increased which indicated the absorption bands of silanol (Si-OH) groups on the zeolite surface and located within the zeolite framework. The peaks at 700-1100 cm\(^{-1}\) showed the vibrations of Si-O and Al-O and 950-1250 cm\(^{-1}\) showed the vibration of the asymmetry Si-O and Al-O from the alumina-silica framework.
Surface morphology and crystal size of calcined ZSM-5 were characterized by SEM. ZSM-5 zeolite synthesized using TPAOH template had coffin-like morphology and hexagonal crystal geometry. Figure 3 showed SEM imaging of ZSM-5_a which clearly visible ZSM-5 zeolite-shaped hexagonal crystal resembling tablets rather than ZSM-5_wa.

The Si/Al ratio of ZSM-5_a and ZSM-5_wa were 18 and 21, respectively. In Figure 4, ZSM-5 zeolite XRD patterns at 2θ between 5-10° indicated a significant peak difference. ZSM-5_a compared with ZSM-5_wa showed low peak while the highest peak appeared in ZSM-5_wa. This result was similar with SEM and EDX results. It can be summarized that ZSM-5_wa has two distinctive ZSM-5 peaks at 2θ position of 7.9-9.11°, three diffraction peaks at the region about 22-25°, and based on SEM-EDX data ZSM-5_wa formed a crystalline structure of ZSM-5. Furthermore, ZSM-5 zeolites were characterized on its pore and surface area using BET instrumentation. According to Table 1, both zeolites had high surface area and based on their pore diameter, they fall into microporous zeolites.
Figure 4. XRD pattern of synthesized ZSM-5 zeolites

Table 1. Textural Parameters of Zeolites

| Samples     | Surface area ($S_{BET}$) (m$^2$ g$^{-1}$) | Average Pore Radius (nm) |
|-------------|------------------------------------------|--------------------------|
| ZSM-5_a     | 262                                      | 1.496                    |
| ZSM-5_wa    | 309                                      | 1.306                    |

4. Conclusions
Microporous ZSM-5 was successfully synthesized using Bayat natural zeolite as partial source of Si and Al. Acidic treatment was not critical as it gave similar ZSM-5 structure and even lower surface area.

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