Bangka Kaolin and Bayat Zeolite-based ZSM-5 zeolite as heterogeneous catalyst for hexadecane cracking reaction

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Abstract. Microporous ZSM-5 material was synthesized using natural aluminosilicate minerals, i.e. Bayat zeolite and Bangka kaolin as silica and alumina sources. Prior to use, Bayat zeolite was treated with several treatments, i.e. purification, fragmentation and dealumination. While Bangka Kaolin was used as the source of additional silica, in which the silica was extracted using aqua regia. After that, ZSM-5 zeolite was synthesized using tetrapropylammonium hydroxide (TPAOH) as template. Then, it was characterized using Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD) and Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX). Based on XRD pattern, mordenite inverted framework (MFI) structure was obtained. SEM-EDX images showed that the natural aluminosilicate-based ZSM-5, so called ZSM-5 MA, has a coffin-like shape with average crystal size and Si/Al ratio are 1.6 μm and 14.26, respectively. As reference, another as-synthesized ZSM-5 was prepared from pro-analysis reagents, and labelled as ZSM-5MS. It also has mordenite inverted framework (MFI) structure, Si/Al ratio of 21.45 and average crystal size of 0.8 μm. ZSM-5 was tested with micro activity test (MAT) method for hexadecane cracking reaction at 500 °C. Prior to be used, the ZSM-5 was subjected to NH3-exchanged followed by calcination at 550 °C to obtain H/ZSM-5. The products that obtained from hexadecane cracking reaction are gas (H2, C–C) and gasoline (C–C) fractions. The catalytic test shows that both H/ZSM-5MA and H/ZSM-5MS gave similar results, despite their differences in Si/Al ratio and particle sizes. Therefore, zeolite synthesis using natural minerals as Si and Al sources is promising to be explored further.

1. Introduction

Fluid catalytic cracking (FCC) is one of the main transformation technologies in the oil refinery industry and generates the main of the world’s gasoline. The demands of gasoline increase the use of this process. Catalytic cracking is a process that have been applied intensively, because of several benefits, such as faster reaction, better product selectivity, and ideal product combustion [1].

One of the most used zeolite in catalytic cracking is Zeolite Socony Mobil-5 (ZSM-5) that has form of mordenite inverted framework (MFI) structure [2]. ZSM-5 is an active catalyst and/or promotes for several processes such as cracking, aromatization, hydrocarbon isomerization, and alkylation because of the activity, structure selectivity, ion-exchange properties, and certain porous structure [3].

Zeolite production occurs in a big scale and usually synthesized using high cost chemical reagent. So, it needs to find an alternative to reduce the cost. Because of that, the research about synthesis zeolite from natural feedstock, such as natural aluminosilicate minerals, fly ash, rice husk, and others are challenging [4–6]. This research focuses on the preparation of microporous ZSM-5 zeolite with...
Bayat zeolite and Bangka kaolin as silica and alumina sources, followed by using it as heterogeneous catalyst for hexadecane cracking.

2. Materials and methods

2.1. Materials.
Bayat zeolite, Bangka kaolin, hydrogen chloride (Merck), nitric acid (Merck), sodium acetate (Merck), acetic acid (Merck), sodium dithionite (Merck), trisodium citrate (Merck), hydrogen peroxide (Merck), sodium hydroxide (Merck), ammonium chloride (Merck), tetrapropylammonium hydroxide (Sigma Aldrich).

2.2. Pre-treatment on Bayat zeolite.
Purification was carried out by mixing Bayat zeolite with buffer acetate pH 5 (1:3) w/v. After that, the mixture was filtered and 200 mL deionized water and 20 mL H.O, were added to the residue. Then, buffer citrate bicarbonate and sodium dithionite were added. After that, the mixture was filtered and dried the residue at 100 °C. Fragmentation was carried out by mixing Bayat zeolite with certain amount of NaOH pellet and deionized water [7], and then heated at 250 °C for 2 h in a furnace. Dealumination was conducted by mixing the Bayat zeolite with 250 mL HCl 2M in the reflux system at 100 °C for 4 h.

2.3. Extracting silica from Bangka kaolin.
Silica extraction was carried out by following the method of Wang et al. [8,9]. First, 100 g Bangka kaolin was heated at 800 °C for 6 h. After that, 40 g Bangka kaolin was mixed with 15 mL deionized water, 280 mL HCl 37 % and 94 mL HNO in the reflux system at 100 °C for 4 h. After that, 90 mL HCl and 30 mL HNO were added into the mixture and continued being refluxed at 100 °C for another 4 h. The precipitate was filtered and washed until its pH was neutral, then dried at 100 °C.

2.4. Synthesis ZSM-5.
Synthesis was carried out by following the published method [8,9]. First, 2.19 g Bayat zeolite was mixed with 5 mL deionized water, and stirred until homogeneous. After that, 10.97 mL TPAOH was added, stirred for 1 h. Then, 0.55 g extracted silica and remaining deionized water was added, stirred for 1 h. After that, pH of mixture was adjusted with glacial CH.COOH until reached pH 11. The mixture was aged at 100 °C for 3 h, and at room temperature for 24 h. The obtained gel was transferred into Teflon-lined autoclave and heated at 170 °C for 6 days. The white precipitate was then washed until pH 8 and calcined at 550 °C for 5 h.

2.5. Modification ZSM-5 become H/ZSM-5.
Modification was conducted by the means of ion-exchange process with 1M of NHCl solution at 60 °C for 12 h. After that, NH/ZSM-5 was calcined at 550 °C for 5 h to obtain H/ZSM-5.

2.6. Application.
Application was carried out using micro activity test (MAT) method. Prior to the reaction, catalyst was heated at 300 °C while nitrogen was flown through the reactor. After that, the reactor temperature was set at 500 °C. Approximately 2 mL Hexadecane was flown for 75 sec. The gas and liquid products were characterized by GC-RGA and GC simulated distillation, respectively.

3. Results and discussion

3.1. Pre-treatment of Bayat zeolite
Based on X-Ray Diffraction (XRD) pattern in Treacy and Higgins [2], it is confirmed that Bayat natural zeolites contains mainly of mordenite structure but has some impurities. Therefore, it was subjected to several treatments to remove the impurities [10]. After that, fragmentation was carried out to breakdown zeolite structure to become its fractions, i.e. SiO$_2$ and AlO$_2$ [7]. Figure 1a shows the results from XRD and figure 1b for infrared measurement. XRD patterns of raw and purified Bayat zeolite are unchanged, while significant change discovered in pattern from defragmented and dealuminated Bayat zeolite. The lost crystallinity and observed amorphous patterns are due to the destruction of Si-O-Al ring during fragmentation, and removal of Al after dealumination, respectively.
Figure 1. (a) Powder XRD patterns and (b) FTIR spectra for Bayat Zeolite (A) raw and after (B) purification, (C) fragmentation and (d) dealumination process

Figure 2. (a) XRD patterns and (b) FTIR spectra for (A) kaolin and (B) extracted silica (from kaolin)

From Fourier Transform Infrared (FTIR) measurement shown in figure 1a spectrum C, it can be seen that new peak was observed in the fragmented Bayat zeolite spectra at 1300 – 1600 cm\(^{-1}\), assigned for NaAlO\(_2\) [5–6]. Energy Dispersive X-Ray (EDX) measurement on final dealumination Bayat zeolite indicates that it contains 34.74% Si, 1.34% Al, 1.39% Na and 63.53% O, to make the Si/Al ratio of 25.9.

3.2. Extraction silica from Bangka kaolin

In order to cover the lack of silica that was required for synthesis, extracted silica from Bangka kaolin was added. Figure 2 shows that both XRD pattern and infrared spectra of extract silica are different from those of original kaolin. In figure 2a pattern A, it can be seen that kaolin has distinct peaks at 2\(\theta\) ≈12.32° and 24.86°, while extracted silica (figure 2a pattern B) has amorphous phase and some peaks were disappeared. Furthermore, infrared spectra from kaolin (figure 2b spectrum A) shows the typical peaks of Si-OH and Al-OH at 3600 cm\(^{-1}\) and 3500 cm\(^{-1}\), respectively [11], indicative of kaolin as phyllosilicate material. They are not observed in extracted silica (figure 2b spectrum B)), but a broad band appeared in 3600–3000 cm\(^{-1}\) instead, assigned for hydrogen-bonded silanol groups [11]. From EDX measurement, the concentrations of Si and Al in extracted silica are 39.71 % and 0.07 %, respectively and the ratio of Si/Al was \(\infty\). This indicates that the extraction process was successfully performed.
3.3. Synthesis of ZSM-5 zeolites

Two microporous ZSM-5 zeolites were synthesized using single template method. One batch used pre-treated Bayat zeolite and extracted Bangka kaolin (called ZSM-5 MA), and as control, another batch was synthesized using pro analysis precursors (labelled as ZSM-5MS). TPAOH was used as template, to obtain MFI structure, since the crystallinity of ZSM-5 was high when using TPAOH as template [12].

Based on XRD pattern in figure 3a, it is shown that as-synthesized ZSM-5MA has MFI structure with the typical peaks at $2\theta = 7^\circ$–$8^\circ$ and $2\theta = 22^\circ$–$25^\circ$ [2]. Furthermore, figure 3b spectrum A shows infrared spectra from ZSM-5MA before calcination with peaks at 2850–2950 cm$^{-1}$ (attributed to $\nu$–CH$_2$) and at 1450–1350 cm$^{-1}$ (attributed to $\delta$–CH$_2$) coming from organic template TPAOH.

EDX analyses provide Si/Al ratio of 14.26 and 21.45, for ZSM-5MA and ZSM-5MS, respectively. The lower Si/Al ratio for ZSM-5MA indicates that the framework has more Al, thus its acidity is higher than the ZSM-5MS [13,14]. From SEM characterization in the figure 4, it can be seen that the crystals of ZSM-5MA also has a hexagonal or coffin-like shape, although not as distinct as that from ZSM-5MS. This is in agreement with typical crystal habit for ZSM-5 [9,15]. In addition, ZSM-5MA has average particle size of 1.6$\mu$m, while ZSM-5MS has smaller size, about 0.8 $\mu$m.

3.4. H/ZSM-5 zeolites

ZSM-5 zeolites were treated with NH$_4$+ multiple-exchange and calcination at 500 °C to obtain H/ZSM-5 zeolites. Figure 5 shows the infrared spectra from ZSM-5 MA, while the spectra from ZSM-5 MS,
Figure 5. FTIR spectra of NH₄/ZSM-5MA (spectrum A) and H/ZSM-5MA (spectrum B)

Figure 6. Graphic of % conversion, % yield and % selectivity from hexadecane cracking product

since similar, were not shown for brevity. Figure 5 spectrum A shows that a broad band at 3200–2800 cm⁻¹ and a sharp peak at 1600 cm⁻¹ were observed, which were attributed to stretching (ν) and bending (δ) vibrations of N-H from NH₄⁺ [16], respectively. After calcination, they disappeared due to ammonia removal, and H/ZSM-5 was obtained (figure 5 spectrum B).

3.5. Cracking reaction application
The materials that tested were natural aluminosilicate-based H/ZSM-5 (H/ZSM-5MA) and H/ZSM-5 synthetic (H/ZSM-5MS). The results of the cracking reaction product are summarized in figure 6. From figure 6, it is suggested that the natural aluminosilicate-based H/ZSM-5 has similar catalytic activity with the synthetic H/ZSM-5. It could happen because the Si/Al ratio of H/ZSM-5MA (14.26) is lower than H/ZSM-5MS (21.45) to compensate the larger particle size of ZSM-5MA (1.6 μm) than that of ZSM-5MS (0.8 μm). Lower Si/Al ratio will increase the cation exchange capacity [15], thus more NH₄⁺ will replace the Na⁺. As consequence, H/ZSM-5MA will be more acidic than H/ZSM-5MS [11].

4. Conclusions
Microporous ZSM-5 was successfully synthesized from Bayat zeolite as silica and alumina sources and Bangka kaolin as additional silica source. Furthermore, it was successfully applied as catalyst in hexadecane cracking reaction, with conversion, yield and selectivity results of 80.49 %; 77.86 % and 96.72 %. The results are comparable to those from synthetic-based ZSM-5 due to benefit of its lower Si/Al ratio and more defective crystal morphology.
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