Synthesis of MnO/ZSM-5 zeolite from natural aluminosilicate minerals and its application as heterogeneous catalyst for α-cellulose conversion to levulinic acid

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Abstract. Microporous ZSM-5 was successfully synthesized using Bayat-Klaten natural zeolite and Belitung kaolin as its mineral source through 2 stages of treatment, i.e. pre-treatment of natural zeolite and kaolin followed by synthesis of ZSM-5 zeolite. Bayat-Klaten natural zeolite as source of Si and Al was first treated as follows: activation, purification, fragmentation, and dealumination, whereas Belitung kaolin as the source of Si, to cover Si deficiency in the synthesis, was treated as follows: activation, purification, and Si extraction. Based on Energy Dispersive X-Ray (EDX) analysis, the Si/Al ratio was 24.8 in dealuminated natural zeolite and 98 % of Si after kaolin extraction. ZSM-5 zeolite was synthesized and characterized using X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR), Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX), and Brunauer-Emmett-Teller (BET) analysis. The XRD pattern showed a similarity with typical ZSM-5 zeolites. Impregnation with Mn(II) followed by calcination at 550 °C giving MnO/ZSM-5 (2.2 wt. % of Mn), that then employed as catalyst for α-cellulose conversion to levulinic acid. High Performance Liquid Chromatography (HPLC) analysis in product reaction showed that the conversion reaction for 6 h resulting in the highest yield of levulinic acid (7.2 %). Therefore, it was revealed that the natural mineral-based ZSM-5 has potential to be used as heterogeneous catalyst.

Keywords: heterogeneous catalyst, levulinic acid, MnO/ZSM-5, natural aluminosilicate, zeolite.

1. Introduction

Nowadays, research about zeolites has been raised due to the uniqueness and benefits of zeolites that can be used in some applications [1]. One of the zeolites that can be used is natural zeolite. However, the utilization of natural zeolite as a catalyst is still limited, because the natural zeolite still has many pollutants that will cause interference in catalyst performance [2–3]. On the other hand, Indonesia has abundant mineral resources such as natural zeolite and kaolin [4]. Therefore, it is necessary to conduct research regarding the appropriate modification and treatment for these minerals so that these natural zeolites can compete with the synthetic zeolites [4–5].

In this study, ZSM-5 zeolite was synthesized from Bayat-Klaten natural zeolite and the silica shortage will be covered from Belitung kaolin, which was previously extracted. ZSM-5 zeolite was then used as catalyst in α-cellulose conversion to levulinic acid [6]. Levulinic acid is a platform chemical derived from glucose degradation from cellulose hydrolysis. Levulinic acid’s production is still captured the scholar’s attention since it has wide range applications [7-9].

2. Materials and methods

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2.1. Materials
Natural zeolite was obtained from Bayat-Klaten, Central Java, Indonesia whereas kaolin was obtained from Belitung, Indonesia. The chemicals used were α-cellulose and tetrapropylammonium hydroxide (TPAOH) purchased from Sigma-Aldrich, levulinic acid (97 %) from TCI, HCl from Smart Lab Indonesia, while NaOH pellets, glacial CHCOOH, H.O. 30 %, Na₂SO₃, NaCH₂O₂, NH₄Cl, H₂SO₄(96 % p.a.), PDDA (34 % p.a.), NaOAc buffer pH 5, Na-citric-bicarbonate, and Mn(II) from E. Merck.

2.2. Pretreatment process of Bayat-Klaten natural zeolite and Belitung kaolin
Belitung kaolin was purified prior extracted, follow published procedure to yield metakaolin [10]. Bayat-Klaten natural zeolite was pretreated in four stages: activation, purification, fragmentation, and dealumination by following the published method [2–3]. Kaolin, metakaolin, and all pretreated natural zeolites in each step were characterized using Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD) and Energy Dispersive X-Ray (EDX).

2.3. Synthesis of ZSM-5 micropore and impregnation of MnO/ZSM-5
ZSM-5 micropore was synthesized by following the published procedures [11]. The synthesized ZSM-5 micropore was then characterized using Scanning Electron Microscopy (SEM), XRD, Brunauer-Emmett-Teller (BET) particle analytical, and FTIR. Impregnation of MnO to ZSM-5 was conducted with Mn(II) 2 % (w/w). Homogenized solution with 1 g of ZSM-5 was made and stirred for 24 h at room temperature until paste formed. The paste was then dried at 60 °C for 1 night, then calcinated for 3 h. MnO/ZSM-5 then was characterized using XRD, FTIR and Atomic Absorption Spectroscopy (AAS).

2.4. α-Cellulose conversion to levulinic acid
α-Cellulose (0.1 g) was mixed with MnO/ZSM-5 (0.01 g), H₃PO₄ 40 % (2 mL), and H₂O 30 % (0.05 mL) in a three-neck round-bottom flask. The mixture was heated under reflux at 130 °C for variation of reaction time (0, 2, 4, 6, 8, and 10 h). A similar reaction was also conducted without the presence of MnO/ZSM-5.

3. Results and discussion
In this study, Belitung kaolin was successfully purified to yield metakaolin. FTIR spectra for the extracted kaolin and metakaolin (figure 1a) showed that raw kaolin tended to have sharp peak because it has an independent SiOH which is not binding to water. Therefore, the peak intensity appeared as wide peak. On the other hand, the extracted silica showed wider peak than raw kaolin because it was interacted with water, resulting a higher peak intensity of H-OH vibration. SEM-EDX result in figure 1b, figure 1c and table 1 proved that after silica extraction, the percentage of silica instantly turned up, while the mole percentage of others were close to zero which caused the Si/Al mole ratio to be infinite.

![Figure 1](image-url)
Table 1. EDX result of kaolin and extracted silica

| Elements | Kaolin | Extracted Silica |
|----------|--------|-----------------|
| Na       | 0.03   | 0               |
| Si       | 17.01  | 39.71           |
| Al       | 17.74  | 0.07            |
| Ratio Si/Al | 0.92 | ∞               |

Figure 2. FTIR spectra for Bayat-Klaten natural zeolite before and after pretreatment process.

Figure 3. SEM image of Bayat-Klaten natural zeolite  
(a) raw, (b) fragmented, and (c) dealuminated.

Figure 2 shows FTIR spectra of Bayat-Klaten natural zeolite in each pretreatment process. Because Bayat-Klaten natural zeolite is an aluminosilicate, it appears vibration for SiO and AlO at wavenumbers of 800-1300 cm⁻¹. Peak at wavenumber of 500 cm⁻¹ was subjected to double ring signified to zeolite structure. Compared with raw Bayat-Klaten natural zeolite, the purified zeolite did not show the peak difference, indicating that purification process did not alter its structure. In fragmented zeolite, it showed new peak at wavenumber of 1500 cm⁻¹ indicating the presence of AlONa⁺ and 1000-1200 cm⁻¹ belongs to SiONa⁺. At wavenumber of 500-600 cm⁻¹, peak of double ring decayed significantly, indicating that structure was successfully decomposed to the monomer form. For dealuminated zeolite, the FTIR spectra showed the similar pattern with raw zeolite because the existing zeolite remain the same, but the intensity of the peak was higher because the purity of zeolite.  

Figure 3 and table 2 exhibited SEM-EDX result of each step of natural zeolite pretreatment. According to figure 3 and table 2, dealumination process was successfully applied in reducing the mole of Al giving the final mole ratio of Si/Al was suitable for ZSM-5 synthesis.
Table 2. EDX results of Bayat-Klaten natural zeolite before and after pretreatment process.

| Elements | Raw  | Fragmented | Dealuminated |
|----------|------|------------|--------------|
| Na       | 0.66 | 23.76      | 1.39         |
| Si       | 34.37| 19.96      | 34.74        |
| Al       | 6.69 | 3.52       | 1.34         |
| Ratio Si/Al | 4.91 | 5.46      | 24.8         |

Figure 4. (a) FTIR spectra of ZSM-5 before and after calcination (b) XRD result of ZSM-5 micropore.

Figure 5. SEM image of (a) ZSM-5 micropore and (b) Mn\textsubscript{3}O\textsubscript{4}/ZSM-5.

FTIR spectra of ZSM-5 before and after calcination are shown in figure 4a. FTIR spectra of ZSM-5 before calcination show a peak at wavenumber of 2960-2850 cm\(^{-1}\) and 1470-1350 cm\(^{-1}\) belongs to vibration of C-H stretching and C-H bending, respectively. These absorption bands come from the template used in ZSM-5 synthesis. This calcination process was performed to remove the organic template. Thus, FTIR spectra of ZSM-5 after calcination showed the loss of template which indicated by the loss of C-H stretching and C-H bending vibration. With calcination, the absorption band at wavenumber of 3600 cm\(^{-1}\) belongs to the absorption band of silanol group (Si-OH) on the surface of the zeolite as well as located within the zeolite (as shown in SEM image in figure 5). The percentage of mass loss after calcination was 14.67 %. In the wavenumber of 700-1100 and 950-1250 cm\(^{-1}\), there were peaks belong to the vibration of Si-O and Al-O which is the framework of aluminosilicate. Furthermore, XRD result of the synthesized ZSM-5 zeolite (figure 4b) proved that this zeolite was successfully synthesized.

To prove that Mn\textsubscript{3}O\textsubscript{4} was successfully impregnated on ZSM-5 zeolite, FTIR spectra was measured (figure 6). According to figure 6, the difference between ZSM-5 and Mn\textsubscript{3}O/ZSM-5 can be observed at wavenumber of 3500 cm\(^{-1}\) indicating the presence of internal Si-OH. Mn\textsubscript{3}O/ZSM-5 zeolite showed a decrease in intensity of Si-OH group compared with ZSM-5 zeolite.
Figure 6. FTIR spectra of MnOx/ZSM-5 zeolite compared with ZSM-5 zeolite.

Figure 7. The percentage yield of levulinic acid analyzed using HPLC.

Figure 7 shows the percentage yield of levulinic acid from α-cellulose conversion. Based on figure 7, MnO/ZSM-5 is able to produce better yield (7.2 %) compared to unimpregnated ZSM-5 catalyst, with the optimum reaction time of 4 h. The Mn impregnated catalyst is better because the metal itself has an active side, so indirectly for the MnO/ZSM-5 has more active side rather than ZSM-5. Therefore, reaction using MnO/ZSM-5 catalyst produced more levulinic acid than the ZSM-5 catalyst. The plausible mechanism for cellulose conversion can be described via hydrolysis followed by isomerization of cellulose to yield fructose then further dehydration to give 5-HMF as intermediate of this conversion [12].

4. Conclusions
Belitung kaolin can be used as Si source to cover the Si deficiency in Bayat-Klaten natural zeolite in order to synthesize the ZSM-5 zeolite, refers to its EDX, SEM, FTIR, and XRD analysis. ZSM-5, zeolite with Si and Al source from kaolin and natural zeolite is capable to replace the synthetic ZSM-5 zeolite and can be used to catalyze α-cellulose conversion into levulinic acid. HPLC analysis showed the highest α-cellulose conversion to levulinic acid was 7.2 % with 4 h of reaction time.
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