Synthesis of hierarchical Fe₂O₃/ZSM-5 from natural minerals as catalyst in partial oxidation of bio-methane

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Abstract. Partial oxidation reaction of bio-methane as a source of methane using ZSM-5 heterogeneous catalyst modified with iron oxide has been carried out. In this study, the ZSM-5 catalyst was synthesized using the double template method using kaolin and natural zeolite as silicate and aluminate sources. The as-synthesized ZSM-5 nat and the Fe₂O₃/ZSM-5 nat catalysts were analyzed using XRD, XRF and BET. The characterization reveals that the synthesis of ZSM-5 was successful and the amount of iron(III) loaded was 2.98 %. The application test of Fe₂O₃/ZSM-5 nat as a catalyst was carried out in stainless steel batch reactor with a certain CH₄ : N₂ feed ratio at 150 °C for 120 min. The reaction products were then analyzed with GC-FID to measure the % yield of methanol product. It is found that Fe₂O₃/ZSM-5 nat catalyst could give 54.93 % yield of methanol. Although the use of bio-methane as feed with lower CH₄ : N₂ ratio, this catalyst was also active and produced 12.26 % yield of methanol.

Keywords: Bio-methane, methanol, iron oxide, partial oxidation reaction, ZSM-5

1. Introduction
Increasing the use of renewable energy becomes the most challenging thing over the number of decades. Some major efforts have been done to investigate and develop an effective route for it. One of the most promising renewable energy is biogas due to the environment and economic factors. Especially in Indonesia, biogas with methane and carbon dioxide as the main component has a tremendous possibility and potential value for a clean-fossil-energy [1].

Biogas is a natural gas produced from an anaerobic process of organic materials such as human, household and animal wastes. The high interest to exploit this natural gas is due to the climate change issue because the flaring natural gas causes carbon dioxide [2]. Activation methane in biogas into value-added chemical such as methanol and hydrogen while reducing the greenhouse effect becomes an eminent challenge for industry through the high stability of C-H bond in CH₄ [3]. Some concepts may have been proposed but it constrained by the technology limitation, not economically feasible for local-small scale facilities and required high energy consumption [4].

Direct partial oxidation can be carried out to convert methane into methanol [5]. However, it has drawbacks to obtain the high selectivity and per cent conversion because of the extreme stability of methane. Some studies proof that catalyst is required in partial methane oxidation reaction [6]. ZSM-5 zeolites show the catalytic activity for selective oxidation of methane [7]. The unique characteristic of zeolite such as pore size, activation procedure and Si/Al ratio becomes important to product selectivity.
Krisnandi et al. [8] conducted a study of two types of cobalt oxide-modified hierarchical zeolite (Co/hierarchical ZSM-5) catalysts which were modified using ion-exchange or impregnation method. Based on this study, the Co-oxide impregnated ZSM-5 catalyst produced the highest conversion compared to the Co-exchanged ZSM-5 catalyst. Furthermore, the microporous Co-oxide/ ZSM-5 counterpart also gave a lower % yield. Nurgita [9] has conducted an experiment using ZSM-5 catalysts modified by various metal oxides, and suggested that Fe and Co oxides produced the highest methanol yield, compared to other transition metals namely Mn and Ni.

Synthesis of ZSM-5 from natural resources, i.e. kaolin and natural zeolite from Indonesia has been carried out in our group [10, 11] modifying a procedure reported by Wang et al. [12]. The novelty of this study was to employ a hierarchical ZSM-5 synthesized from natural sources, modify with Fe$_2$O$_3$, in similar partial oxidation of methane to methanol. In addition, bio-methane was also introduced as feed in the reaction, in order to observe the feasibility of the partial oxidation reaction using bio-methane.

2. Materials and method

2.1. Materials
Natural Bayat zeolite, Belitung kaolin (PT. Aneka Kaoline Utama), distilled water, bio-methane (methane 83.7 % and oxygen 16.3 %, PT. Swen Inovasi Transfer), hydrogen chloride (PT. Smart Lab Indonesia), nitric acid, sodium hydroxide pellets, glacial acetic acid, 30 % hydrogen peroxide, sodium ditionite, sodium acetate, tri sodium citrate, ethanol, glacial acetic acid (Merck), tetra propyl ammonium hydroxide, poly(acrylamidialildymethylammonium chloride), Fe(NO$_3$)$_3$.9H$_2$O (Sigma Aldrich), methane p.a. 99.9 %, oxygen gas, nitrogen gas (CV. Retno Gas).

2.2. Pre-treatment of natural Bayat zeolite and Belitung Kaolin
Natural Bayat zeolite was treated through an activation process by dissolving zeolite in distilled water with ratio 1:3 (w/v), then the zeolite was purified by adding Na-acetate buffer solution with 1:3 (w/v). Fragmentation process was done through sub-molten salt (SMS) system by using NaOH pellets with molar ratio 2:1 (w/w) in deionized water.

2.3. Synthesis of hierarchical ZSM-5 and ZSM-5
Hierarchical ZSM-5 zeolite was synthesized using natural Bayat zeolite as the natural source of silicate and aluminate. In addition, silica extracted from kaolin was added as an additional source of silica. Hierarchical ZSM-5 synthesis was carried out by referring to the mole composition of Wang et al. [12]. Poly dimethyl diallyl ammonium chloride was added at room-temperature process as the secondary template and stirred for 24 h before transferred into Teflon-lined autoclave. The obtained zeolite was labelled as ZSM-5 nat.

2.4. Preparation and activation of natural Fe$_2$O$_3$ / ZSM-5 catalysts
The as-synthesized hierarchical ZSM-5 nat catalyst was mixed with Fe(III) solution of 0.2495 M through the impregnation method. Characterization of both as-synthesized and modified ZSM-5 was carried out using Powder X-ray diffraction (PXRD) in Shimadzu 6000, with Cu-K radiation ($\lambda = 1.54184 \text{ Å}$) and $2\theta = 4–70^\circ$ (step width 0.02° in $2\theta$) and operated on 40 kV and 30 mA, and the NOVA 2200e SAA analyzer using the BET method using adsorption / desorption. The ZSM-5 which has been impregnated with iron oxide, was characterized using XRF to determine the % loading of metal impregnated into the ZSM-5.

2.5. Methane partial oxidation application test
Typical catalytic test procedure [8] was carried out in a batch reactor of 200 mL stainless steel vessel. The application of bio-methane, as a source of CH$_4$ gas, was also carried out with bio-methane: N$_2$ ratio is 0.2:2 bar. The measurement of product concentration was carried out by the standard addition method.
Analysis of reaction results was carried out using GC-FID Shimadzu 2010 which was equipped with a carbowax column to determine the methanol from the reaction product.

3. Results and discussion

3.1. XRD characterization of raw material

The natural zeolite as aluminate and silicate sources needs to be pre-treated (activation and purification) process to remove impurities. Then, the fragmentation process was performed to breakdown the zeolite structure. Figure 1a shows that the raw and purified zeolites contain a typical pattern of mordenite structure at 2θ of 9.85°, 22.21° and 25.61° [13]. All those peaks were not observed in the fragmented zeolite. It can be concluded that the fragmentation process was done successfully. Figure 1b shows the comparison between kaolin, metakaolin and extracted silica indicating that the extraction process has been done successfully because the pattern of amorphous extracted silica is different from the initial kaolin.

3.2. XRF analysis of raw material

Table 1 gives information about the composition about ratio Si and Al (Si/Al) from zeolite, kaolin and extracted silica. It can be seen that fragmented natural Bayat zeolite has 9.79, kaolin has 0.85 and extracted silica has 12.02 for Si/Al ratio.

3.3. XRD Characterization of ZSM-5 nat

Figure 2 shows that XRD result of ZSM-5 nat has typical peaks of MFI structure at 2θ of 7°–10° and 22–25° [14]. The XRD result is also compared with the International Zeolite Association (IZA) Online

![XRD patterns of silicate and aluminate sources, before and after pre-treatment](image)

(a) Natural Bayat zeolite, and (b) Kaolin.

| Table 1. XRF analysis of natural zeolite, kaolin, extracted silica and ZSM-5 nat. |
|----------------|
| **Element** | **Fragmented natural Bayat zeolite** | **Kaolin** | **Extracted silica** | **ZSM-5 nat** |
| Si | 57.19 | 57.11 | 84.985 | 71.66 |
| Al | 5.84 | 66.78 | 7.070 | 4.23 |
| Si/Al | 9.79 | 0.85 | 12.02 | 16.94 |
structure database [15] and shows a similar pattern of ZSM-5. So, it can be concluded that the synthesis of ZSM-5 nat has already performed successfully. It also shows XRD pattern after impregnation iron oxides on ZSM-5 nat indicating the typical peaks for hematite iron oxide compounds on ZSM-5 material at 2θ of 30°, 42° and 64° [16].

3.4. Elemental analysis
Elemental analysis from XRF data shows that ZSM-5 nat has Si/Al ratio of 16.94. Furthermore, the percent loading of Fe(III) in Fe₂O₃/ZSM-5 nat was 2.98 %.

3.5. Surface area analysis
From table 2, it can be seen that modification of Fe₂O₃ in ZSM-5 nat did not affect the total surface area of ZSM-5 nat. However a closer look at the composition of micropore/ mesopore, there is a decrease in micropore surface area and increase in mesopores counterpart. This indicates that some of Fe₂O₃ clusters were created inside the micropore while some others aggregated on the external surface and created new mesoporosity.

3.6. Catalytic test
Figure 3 shows the chromatogram of methanol and ethanol from partial oxidation with retention time of methanol is 3.2 and ethanol is 3.4.

Table 3 shows the %yield of methanol by using methane p.a. and bio-methane as feeds in the partial oxidation reaction. The reaction using methane p.a has given a 54.93 %yield, which is comparable with the result from a similar reaction using Fe₂O₃/ZSM-5 prepared from pro analysis precursors [17].

![Figure 2. XRD diffractogram for ZSM-5 nat, and Fe₂O₃/ZSM-5 nat.](image)

### Table 2. Surface area analysis of ZSM-5 nat and Fe₂O₃/ZSM-5 nat.

| Materials       | Surface area (m²/g) | Micropore surface area (m²/g) | Mesopore surface area (m²/g) | Total pore volume (cc/g) | Micropore volume (cc/g) | Mesopores volume (cc/g) | Pore radii (nm)  |
|-----------------|---------------------|--------------------------------|-------------------------------|--------------------------|-------------------------|--------------------------|----------------------|
| ZSM-5 nat       | 234.5               | 215.0                          | 19.46                         | 0.1611                   | 0.1608                  | 0.0003                   | 1.89178              |
| Fe₂O₃/ZSM-5 nat | 234.5               | 199.9                          | 34.69                         | 0.1404                   | 0.09866                 | 0.04174                  | 1.90324              |
Figure 3. Chromatogram of methanol and ethanol.

Table 3. Characterization for partial oxidation of bio-methane catalytic test.

| Catalyst | % yield methanol | Methane p.a. (0.75 atm)* | Bio-methane (0.2 atm)* |
|----------|------------------|--------------------------|------------------------|
| 0.5 gram Fe₂O₃/ZSM-5 Nat | 54.93 | 12.26 |

*N₂ feed: 2 atm

Due to the limitation of bio-gas pressure (only available at 1 atm), the bio-methane:N₂ ratio was only 0.2:2 compared to the methane p.a:N₂ ratio of 0.75:2. Nevertheless, the partial oxidation of biomethane has produced a methanol yield of 12.26%.

4. Conclusion
Partial oxidation of bio-methane over Fe₂O₃/ ZSM-5 nat has been carried out successfully. ZSM-5 nat could be employed as support to iron(III) oxide active catalyst. Furthermore, the catalytic test shows the potential to utilize the bio-methane in methane conversion to methanol.

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