Synthesis of metal oxide-hierarchical ZSM-5 (Co$_3$O$_5$/ZSM-5 and Fe$_3$O$_5$/ZSM-5) as catalysts for partial oxidation of biomethane to methanol

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Abstract. This study presents a partial oxidation of biomethane from anaerobic organic waste of cow dung (83.7 % of methane and 16.3 % of oxygen) to methanol using modified cobalt and iron metal oxide-hierarchical ZSM-5 catalysts. Hierarchical ZSM-5 was synthesized using double template methods with tetrapropylammonium hydroxide (TPAOH) and dimethyl dially ammonium chloride acrylamide copolymer (PDDAM) as the first and secondary templates, respectively. The as-synthesized ZSM-5 materials were characterized with Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDS), Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD), and the results show the similarities of physicochemical properties with standard ZSM-5 materials. The hierarchical ZSM-5 was then modified with cobalt or iron oxides through impregnation with incipient wetness. The results of XPS analysis show that the impregnated cobalt and iron metal oxide are CoO and FeO, respectively. While the AAS analysis indicates that the metal content in CoO/ZSM-5 and FeO/ZSM-5 are 2.1 % (Co) and 2.4 % (Fe), respectively. The partial oxidation of bio-methane to methanol was carried out in an atmospheric fixed batch reactor, c.a. 200 mL, with biomethane to N ratio of 0:2:2 (in bar). The results of application using biomethane show the hierarchical FeO/ZSM-5 catalyst has higher methanol yield (17.61 %), compared to the yield by using hierarchical CoO/ZSM-5 (10.99 %). In addition, no side product is detected after reaction. Thus, it can be concluded that FeO is more active than CoO, as catalyst and biomethane can be utilized as source in this partial oxidation reaction.

Keywords: bio-methane, metal oxide, methanol, partial oxidation, hierarchical ZSM-5

1. Introduction

Nowadays, many of the world's interest is environmentally friendly renewable energy sources as a result of the limited fossil fuel resources, given the increasing energy needs. Biogas is one of the most promising renewable energy sources in terms of environmental and economical factors [1]. Biogas is generally produced from anaerobic organic waste derived from the environment such as livestock’s manure. Biogas contains methane and carbon dioxide as the largest component, and small amounts of nitrogen, oxygen, hydrogen sulfide, halogen, and aromatic compounds.

Utilization of methane gas can be done by methane reforming process to get syngas, and converting to methanol with partial oxidation reaction. Methane conversion through partial oxidation reactions can be done directly. However, this direct conversion has drawbacks, given that methane is a stable compound and requires high temperatures and is suitable for making methane to be unstable in order to be converted into other compounds with high percent conversion and high selectivity rates [2]. Thus, a catalyst, which can be used in the partial oxidation reaction of methane, is required. Catalytic oxidation of methane with N,O using Fe-zeolite systems, in order to optimize methane conversion activity was reported [3]. However, N,O gas is rather difficult to handle, compared to molecular O, or...
even air. Beznis et al. [2] reported the methane oxidation into methanol and formaldehyde through Co–ZSM-5 zeolite agglomerates, by adjusting the reactivity and selectivity using alkaline and acid treatments on the zeolite. Krisnandi et al. [4] used a hierarchical Co-oxides/ZSM-5 catalyst, and the reaction showed a high selectivity toward methanol conversion. Furthermore, partial oxidation of methane over hierarchical H-ZSM-5 modified with cobalt oxide species has also been carried out [5]. In this work, we used a biogas (biomethane) as a methane source for partial oxidation of biomethane to methanol using Co,O/ZSM-5 and Fe,O/ZSM-5 catalysts.

2. Experimental

2.1. Materials

For synthesis of hierarchical ZSM-5 the materials needed were tetraethyl orthosilicate (TEOS, 98%, Sigma Aldrich), sodium aluminate (Sigma Aldrich), tetrapropylammonium hydroxide (TPAOH, 1 M, Sigma Aldrich), dimethyl diallyl ammonium chloride acrylamide copolymer (PDDAM, 10 wt%, Aldrich), and deionized water. For modification with metals oxide the materials needed were cobalt (II) nitrate (Co(NO$_3$)$_2$·6H$_2$O, Sigma Aldrich), iron(II) nitrate (Fe(NO$_3$)$_3$·9H$_2$O, Sigma Aldrich). For the catalytic test the materials needed were bio-methane (anaerobic organic waste derived from livestock’s manure, PT SWEN IT Ciomas-Bogor), methane gas (99.99% UHP from BOC), and N, gas (99.99 % UHP).

2.2. Synthesis of hierarchical ZSM-5

The hierarchical ZSM-5 was prepared by hydrothermal reaction using Wang et al. [6] methods with some modifications. All the materials with molar ratio of 1 AlO : 64.34 SiO : 10.07 (TPAOH : 3571.70 H$_2$O were mixed under stirring at 373 K for 3 h. The PDDAM was added slowly and stirred at the ambient temperature for 48 h. The hydrothermal reactions were carried out in an autoclave at 443 K for 144 h. The product was filtered and dried at the ambient temperature. Activation ZSM-5 by calcination at 823 K. The hierarchical ZSM-5 was characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR, Shimadzu Prestige 21) and Scanning Electron Microscopy with Energy Dispersive X-ray (SEM-EDX, SEM FEI quanta FEG 450).

2.3. Preparation of M,O/ZSM-5

Metal oxide–hierarchical ZSM-5 (M,O/ZSM-5) was prepared using wet impregnation methods. 1 g of ZSM-5 was mixed with 0.2495M metal nitrate solution and stirred at the ambient temperature for 24 h. The activation of M,O/ZSM-5 by calcination at 823 K. The catalysts were characterized by XRD and atomic absorption spectroscopy (AAS) instrument.

2.4. Biomethane analysis

The biomethane used in this research was from anaerobic organic waste derived from livestock’s manure (PT SWEN IT Ciomas-Bogor). The composition of bio-methane was analyzed using Gas Chromatography – Mass Spectrometry (GC-MS Shimadzu QP 2010 Ultra).

2.5. Catalytic test: partial oxidation of bio-methane

The partial oxidation of bio-methane tested for its catalytic property was performed in atmospheric fixed batch reactor. The amount of Co,O/ZSM-5 and Fe,O/ZSM-5 catalysts used was 0.5 g. The reaction of catalytic test was performed at 423 K for 2 h with composition of bio-methane and nitrogen pressures of 0.2 and 2 bar, respectively. The product was extracted with ethanol and analyzed using gas chromatography (GC, Shimadzu 2010 FID Detector).

3. Results and discussion

3.1. Characterization of hierarchical ZSM-5

In this method the TPAOH template was used as a directing structure of MFI, which is a structural type of ZSM-5. The alumina source in synthesis of ZSM-5 was obtained from NaAlO$_2$, while the silica source was obtained from TEOS, and the PDDAM was used as a mesopore template. The positively charged PDDAM can interact with the negatively charged of ZSM-5 materials, so the ZSM-5 framework could be established around the PDDAM [6]. The standard ZSM-5 material has a typical diffraction pattern on 20 between 7–10° and 22–25° [7]. The XRD pattern of as-synthesized
Hierarchical ZSM-5 (figure 1) shows certain peaks in the 2θ range from 7° to 10° and from 22° to 25°, which is consistent with the standard ZSM-5 pattern, indicating that the ZSM-5 structure was successfully synthesized.

The FTIR spectra of ZSM-5 in before and after activation by calcination at 823 K are shown in figure 2. The spectrum of ZSM-5 before activation shows several extra peaks at 2960–2850 cm⁻¹ which is C–H stretching, and at 1475–1350 cm⁻¹ is C–H bending, compared with the ZSM-5 after activation, which can be attributed to the templates used in the synthesis of ZSM-5 material, i.e., TPAOH and PDDAM. Calcination process was used to remove the organic templates in the synthesis of ZSM-5 material. It can be seen that the template was removed as indicated by the loss of the C–H stretching and C–H bending vibration bands. Moreover, the pores and channels in the zeolite became empty after calcination.
Figure 3. SEM analysis for Hierarchical ZSM-5

Figure 4. XRD patterns of (a) CoO/ZSM-5, and (b) FeO/ZSM-5

SEM-EDX was used to determine the crystal structure by the morphology and the Si/Al ratio of the synthesized ZSM-5. In agreement with the standard ZSM-5 morphology [8], figure 3 presents the morphology of as-synthesized hierarchical ZSM-5 has hexagonal or coffin-shaped. Rough surface observed in ZSM-5 indicates the loss of PDDAM template used in the hierarchical ZSM-5 synthesized. The EDX analysis was performed to determine the composition and quantity of elements of a material. It can also be used to determine the Si/Al ratio of ZSM-5 material. By the results, the Si/Al ratio on as-synthesized ZSM-5 material was 27.

3.2. Preparation of M,O/ZSM-5

M,O/ZSM-5 heterogeneous catalysts were synthesized using a wet impregnation method, then the activation of catalysts with calcination up to 823 K. The elemental analysis with AAS indicates the distribution of metals (% weight loading) in ZSM-5 material. It was about 2.1 % and 2.5 % for CoO/ZSM-5 and FeO/ZSM-5, respectively. Figure 4 shows the XRD patterns of modified ZSM-5 catalysts. The results of XRD analysis also show the similarity of diffraction patterns for the modification of cobalt and iron metal oxides in the hierarchical ZSM-5 which is in the diffraction pattern with high intensity at 2θ of 7–10° and 22–25°. The similarity indicates that the process of metal oxide impregnation in ZSM-5 material does not damage the material structure of ZSM-5. However, the modification of the metal oxide into the ZSM-5 material causes a decrease in the crystallinity of the ZSM-5 material. This is due to the interaction between metals with the ZSM-5 framework. Figure 4a shows the diffraction patterns at 2θ = 31°, 45°, 55° and 60° attributed to CoO, [9]. Moreover, at figure 4b the diffraction pattern at 2θ = 30°, 42° and 64° are attributed to FeO.[10].
### 3.3. Biomethane component

Biogas is one of the most attractive sources of environmentally friendly renewable energy and its exploitation is very economically beneficial [1]. Biogas used in the application of partial oxidation of methane to methanol, produced from anaerobic organic waste derived from livestock’s manure. Biomethane was transferred from the supplier using biogas bag made of thick synthetic rubber. The biomethane was analysed by using Gas Chromatography-Mass Spectrometry (GC-MS) instrument to determine the composition of the biomethane. Table 1 shows the content of the compounds in the biomethane sample derived from livestock’s manure, i.e., methane and oxygen gas. Based on this result, biomethane contains only methane and oxygen, which can be used as feed without further purification.

### 3.4. Methane partial oxidation catalytic test

The results of biomethane partial oxidation using as-synthesized ZSM-5 catalysts are shown in figure 5. From those results, it can be observed that the catalysts modified in the hierarchical ZSM-5 modified with the cobalt and iron metal oxide was selective to methanol production. This is consistent with our previous results [4,5]. However, the amount of methanol yield obtained in the biomethane partial oxidation reaction is smaller than that of methane p.a. This may be due to the amount of biomethane feed into the reactor was smaller, carried out manually by pressing the bio-methane from poly-bag. Based on the process, the maximum pressure of bio-methane gas that could enter into the reactor is only 0.2 bar and the optimum reaction condition (pressure = 0.75 bar) could not be reached. The oxygen content in the biomethane also increases the yield of methanol, which also in consistency with the previous results [5]. The metals oxides impregnated in ZSM-5 are capable of being the active site of the catalyst for oxidizing methane to methanol. The finding in this work is the Fe$_2$O$_3$/ZSM-5 catalyst gives the highest % yield of methanol than CoO/ZSM-5 catalyst.

### 4. Conclusions

Hierarchical ZSM-5 modified by cobalt and iron oxides could be used as catalysts in partial oxidation of biomethane. Biogas, which derived by anaerobic organic waste, could be used as methane source in partial oxidation biomethane. Modified cobalt and iron oxides-hierarchical ZSM-5 catalysts were selective to methanol production. The catalytic test using biomethane shows that the hierarchical Fe$_2$O$_3$/ZSM-5 catalyst gives the highest methanol yield i.e. 17.61%.

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**Table 1. The Bio-Methane Component**

| Component | Concentration |
|-----------|---------------|
| Methane   | 83.7%         |
| Oxygen    | 16.3%         |

**Figure 5.** Results of partial oxidation of methane using metal oxide-modified ZSM-5
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