Hierarchical ZSM-5 synthesized from Bangka kaolin and Bayat natural zeolite for methane conversion catalysts

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Abstract. Hierarchical ZSM-5 has been successfully synthesized from Bayat natural zeolite as alumina and silica source and Bangka kaolinite as an additional silica source using tetrapropylammonium hydroxide (TPAOH) and poly(acrylamide-co-dialyldimethylammonium chloride) (PDDA-M) as a structure and pore directing agent. XRD pattern shows an evidence of MFI (Mordenite Inverted Framework) structure with peaks at 2θ = 8.01°, 8.90° and 23.15°. SEM images show that the surface of as-synthesized zeolite has coffin-like structure, while EDX analysis shows it has a Si/Al molar ratio of 8.77. The N2 isotherm adsorption exhibited a type IV H4 curve, which indicated the material has mesoporosity, although the Barrett-Joyner-Halenda analysis showed the ZSM-5 has a pore size distribution around 1.937 nm, indicated the micropore dominating its pore size. This confirms that the as-synthesized natural ZSM-5 has hierarchical properties. This as-synthesized natural ZSM-5 then was impregnated with Fe2O3 to improve its catalytic activity towards methane conversion reaction. XRD analysis shows an existence of Fe2O3 at 2θ = 41.22°. Both Fe-impregnated synthetic and natural ZSM-5 show a higher percentage of methane conversion (84.825 % and 86.958 %, respectively), but they give a lower percentage yield of formaldehyde (39.973 % and 32.2 %, respectively) than the parent synthetic and natural ZSM-5.

Keywords: Hierarchical ZSM-5, green synthesis, partial oxidation, methane

1. Introduction
Natural gas has a very important role in fulfilling energy needs in the future because of its enormous abundance in nature. Indonesia has very large natural gas reserves, according to PT Perusahaan Gas Negara (2015), Indonesia has proven and potential natural gas reserves of 103 Tcf (trillion standard cubic feet) or about 3 million cubic meters [1]. Most components of natural gas comprise methane (~95 %) and other gases (~5 %). On the other hand methane is one of the gases that cause the greenhouse effect if released into the atmosphere [2].

Although methane gas is a potential energy source, the production and use of methane faces several obstacles, one of which is the difficulties in terms of transportation. Because of its low density (10.75 kWh per cubic meter), methane needs to be compressed at 10–100 atm in order to be transported, this process is still relatively expensive and inefficient [3]. For this reason, it is necessary to develop catalysts that can convert methane gas into liquids in a more efficient way. One way that can be taken is to convert methane to methanol.
Methanol is a liquid that can be easily transported with the existing infrastructure. Moreover, methanol has many benefits such as being used in fuel cells, converted to gasoline or diesel fuel, and used as a precursor to various chemicals [4].

Kaolin is a very abundant mineral discovered in Indonesia. According to data from the Directorate General of Mineral and Coal in the 2015 Indonesia Mineral & Coal Information document, the abundance of kaolin in Indonesia recorded as of 2015 amounted to 1,070,015,564 tons [5]. The abundance of kaolin is spread in Banten Province, Bangka Province and West Kalimantan Province. Kaolin is a clay mineral (clay) with the molecular formula of \( \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \) and has a high content of Si and Al atoms which is useful in the synthesis of aluminasilicate minerals [6]. Kaolin has been widely used as a source of silica in the synthesis of zeolites, including SAPO, zeolite A, zeolite X and mordenite [7]. Kaolin has also been used as a raw material for ZSM-5 zeolite synthesis through the methacholine dealumination method resulting from calcination of kaolin at 600 °C for 6 min [8] and also with the addition of an additional silica source SiO\(_2\) sol (40 % wt) [9]. The abundance of kaolin in Indonesia as well as the potential use of kaolin in the synthesis of aluminosilicate minerals, especially zeolites, need to be utilized.

Natural zeolites are volcanic products that freeze into volcanic rocks, sedimentary rocks and metamorphic rocks which then undergo weathering processes due to the external influences such as temperature. Indonesia has 500 volcanoes, of which 127 are active (Geological Agency of the Ministry of Energy and Mineral Resources). This data means that there is a potential abundance of natural zeolites from the physical processes of volcanic activity in volcanoes in Indonesia. Some types of natural zeolites formed include clinoptilolite, mordenite, phillipsite, chabazite and laumontite. Natural zeolite is found in different compositions, especially from the composition of the Si/Al ratio and the type of metal which is a minor component [9]. One of the abundant natural zeolites is natural zeolites originating from Bayat district, Klaten regency, Central Java. Bayat natural zeolite has been known to have a Si/Al ratio of 11 with a SiO\(_2\) content of 79.1 % and Al\(_2\)O\(_3\) of 7 % [10].

ZSM-5 synthesis has often been carried out with various alumina and silica sources such as sodium aluminate (NaAlO\(_2\)), tetraortosilicate (TEOS), ludox and others. However, the use of pro-analysis materials as raw material for synthesis is economically less profitable, so the use of natural materials as a source of alumina and silica is a promising alternative. This paper discusses the preparation of ZSM-5 from natural sources and its application as catalyst after modified with iron-oxides, in partial oxidation of methane. The results are compared to the similar reaction using as-synthetic ZSM-5 from pro-analysis precursors.

2. Materials and method

2.1. Materials

Indonesian kaolin from Bangka island was purchased from PT Aneka Kaoline Utama (Bangka Island, Indonesia), Bayat natural zeolite, tetrapropylammonium hydroxide (TPAOH, 40 %, Merck), sodium aluminate (Sigma Aldrich), tetraethyl orthosilicate (TEOS, 98 %, Sigma Aldrich), poly(acrylamide-co-diallyldimethylammonium chloride) (PDDA-M), CH\(_3\)COOH (glacial, Merck) and deionized water are used for ZSM-5 synthesis, while iron (III) nitrate (Fe(NO\(_3\))\(_3\).9H\(_2\)O, Sigma Aldrich) is used to prepare Fe\(_x\)O\(_y\)/ZSM-5. Methane gas (99.9 % BOC, CV Retno Gas), nitrogen gas (99.99 % UHP, CV Retno Gas) and mixed gas (nitrogen 99.5 % mixed with oxygen 0.5 %, CV Retno Gas) are used for methane partial oxidation reaction.

2.2. Natural zeolite and kaolin pre-treatment

Bayat natural zeolite and Bangka kaolin were processed through several pre-treatment steps before ready to use as starting material for ZSM-5 synthesis [11]. Each of them was sieved until 100 μm and dispersed in water (1:3 w/v). The mixture was stirred, decanted and dried at 300 °C for 2 h. Then, it was purified based on Ming and Dixon method [10], and fragmented using calcination process at 800 °C for 6 h.
The silica was collected from fragmented kaolin by using aqua-regia solution. The solution was
decanted, and sediment was washed and dried in an oven at 100 °C for 2 h.

2.3. Synthesis of hierarchical ZSM-5
Synthesis of hierarchical ZSM-5 from natural sources was conducted using Bayat natural zeolite as
aluminate and silicate source and Bangka kaolin as an additional silicate source. Initially, both of Bayat
natural zeolite and Bangka kaolin were mixed with H2O then stirred at room temperature for 24 h. After
that, TPAOH was slowly added into Bayat natural zeolite suspension under vigorous stirring. After that,
Bangka kaolin suspension was added to the mixture. Then, the pH solution was adjusted until ±11 using
glacial acetic acid and then stirred at 373 K for 3 h. Afterward, the mixture was cooled down to room
temperature and then a certain amount of PDDA-M solution was added dropwise into the mixture and
stirred for 48 h, then hydrothermally processed in a Teflon-lined stainless steel autoclave with a volume
of 200 mL at 423 K for 144 h. Then, the obtained white powder was filtered and dried at room
temperature before calcined at 823 K for 3 h. On the other hand, synthetic hierarchical ZSM-5 synthesis
method was adopted from the procedure by Wang et al. [12] with some modifications. NaAlO2 and
TEOS were used as the aluminate and silicate respectively source with a mole ratio of 1 Al2O3:64.3469
SiO2:10.0768 (TPA)2O:3571.66 deionized water. Both as-synthesized synthetic and natural ZSM-5 were
characterized using FTIR (Bruker Transmission Alpha), XRD (Rigaku Smartlab), surface area analyzer
(Quantachrome QuadraWin 2000-16) and SEM-EDX (JEOL JSM-GG510LA).

2.4. ZSM-5 surface modification
Fe2O3/ZSM-5 was prepared using a wet impregnation method. Initially, a desired amount of Fe3+
0.2495 M (from Fe(NO)3.9H2O), was added dropwise into ZSM-5 to make 2.5 wt% of Fe content.
The solution was stirred overnight at room temperature followed by calcination at 550 °C for 3 h. Both
synthetic and natural Fe2O3/ZSM-5 were characterized using XRD (Rigaku Smartlab), surface area analyzer
(Quantachrome QuadraWin 2000-16) and SEM-EDX (JEOL JSM-GG510LA).

2.5. Partial oxidation of methane reaction
Partial oxidation of methane was conducted in a batch reactor with an internal volume of 300 mL.
Each reaction was carried out with 0.5 gr of catalyst, 0.75 atm of methane gas and 2 atm of nitrogen gas
(containing 0.5 % oxygen) with reaction time of 120 min and reaction temperature of 150 °C. The catalyst used were as-synthesized synthetic ZSM-5, as-synthesized natural ZSM-5, and both modified Fe2O3/ZSM-5 derivates. Determination of methane gas before and after reaction was carried out with Gas Chromatography (GC) instrument (Shimadzu-8A), with Porapaq Q and Molecular Sieve 5A column and TCD detector. After the reaction finished, the reactor was cooled down to room
temperature and 3 mL of ethanol was injected to the reactor to extract the product from the catalyst. The
product was analyzed using GC instrument (Shimadzu-2014) with RTX-5 column and FID detector.

3. Results and discussion

3.1. Pre-treatment of natural zeolite

3.1.1. Pre-treatment of Bangka kaolin. Figure 1 illustrates the wide-angle powdered XRD spectra of
pre-treated kaolin. The raw Bangka kaolin pattern (brown line) shown in figure 1 confirms the identity
of kaolinite [13]. The material showed a strong diffraction peak at 2θ = 10–15°, some weaker diffraction
peaks at 2θ = 24–26° and weak diffraction peaks at 2θ = 33–41°. After thermal treatment of purified
kaolin at 800 °C for 6 h yielded metakaolin, characteristic peaks for kaolinite at 2θ = 10–15° and
2θ = 33–41° disappear, while peaks assigned to quartz (2θ = 20–21° and 2θ = 26–27°) remains
unchanged [14]. After acid treatment of metakaolin with aqua regia to extract the silica, characteristic
peaks for quartz remains unchanged.
3.1.2. Pre-treatment of Bayat natural zeolite. Figure 2 illustrates the wide angle powdered x-ray diffractogram of pre-treated Bayat natural zeolite. The raw ZAB pattern (red line) shown in figure 2 confirms the identity of mordenite structure. The material showed a diffraction peak at $2\theta = 8–11^\circ$ and $2\theta = 20–30^\circ$. After treatment of purified ZAB yielded fragmented ZAB, those diffraction peaks still remain unchanged, indicate there is no structural change after the treatment.

3.2. ZSM-5 synthesis from analytical grade and natural source

3.2.1. Structure and morphology. All the wide-angle powdered x-ray diffractogram of synthetic and natural ZSM-5 as well as their modified derivatives with iron oxide are shown in figure 3. Natural ZSM-5 synthesized from Bayat natural zeolite and Bangka kaolin exhibited the characteristic peaks correlated with ZSM-5, which means ZSM-5 zeolite had been successfully synthesized. After impregnation with iron oxide, there is a weak diffraction peak at $2\theta = 40–42^\circ$ which correlated to Fe$_2$O$_3$ species. These peaks appearance means the impregnation had been done successfully.

![Figure 1. X-Ray Diffractogram of pre-treated kaolin. K = kaolinite, Q = quartz.](image1)

![Figure 2. X-ray Diffractogram of pre-treated Bayat natural zeolite (ZAB).](image2)
SEM images of synthetic ZSM-5 and natural ZSM-5 are shown in figure 4. Both samples (a and b) show a hexagonal coffin-like morphology, which is the characteristic of ZSM-5 [15]. However, the shape shown in figure 4a is more uniform which is different from figure 4b. It can be seen in figure 4b that the shape is a little bit irregular which only happens in zeolite synthesized from natural mineral. After impregnation with iron oxide, as shown in figure 4c and figure 4d, the material still shows the same morphology which means the impregnation do not affect the material morphology.

Figure 3. X-ray Diffractogram of as-synthesized (a) synthetic ZSM-5 and natural ZSM-5, (b) Fe₂O₃/ZSM-5 derivates.

Figure 4. SEM images of (a) synthetic ZSM-5, (b) natural ZSM-5, (c) natural Fe₂O₃/ZSM-5 and (d) synthetic Fe₂O₃/ZSM-5 with a magnitude of 10,000x.
The elemental analysis of the as-synthesized synthetic ZSM-5 and natural ZSM-5 determined with EDX instrument is shown in table 1. The as-synthesized synthetic ZSM-5 and natural ZSM-5 has Si/Al ratio of 23.16 and 8.18, respectively. Table 1 also shows the atomic percent of Fe in Fe₂O₃/ZSM-5 of about 1.23 % in synthetic ZSM-5 and 2.42 % in natural ZSM-5. Higher Fe-atomic percentage in natural ZSM-5 than in synthetic ZSM-5 is correlated to its lower Si/Al ratio, because lower Si/Al ratio increases the amount of the Brønsted acid sites so it could be capable to accommodate more Fe atom [16].

BET analysis was used to determine the materials textural parameter such as surface area, pore size distribution and pore volume using Brunauer-Emmett-Teller equation. The surface area of synthetic ZSM-5 and natural ZSM-5 in order of 281.418 m²/g and 168.765 m²/g, respectively. After impregnation with iron oxide, the surface area of synthetic Fe₂O₃/ZSM-5 and natural Fe₂O₃/ZSM-5 decreased to 219.503 m²/g and 165.875 m²/g, respectively. This indicates that some iron oxides have grown inside the pores.

The N₂ adsorption-desorption isotherms at -196 °C for synthetic ZSM-5 and natural ZSM-5 are shown in figure 5a. As it can be seen, both of the N₂ adsorption-desorption isotherm displays a type-IV H4 profile which is the characteristic of hierarchical materials [17]. It can be also seen in figure 5a, after impregnation with iron oxide, the curve remains the same which means the impregnation do not change the pore characteristics of the materials.

The textural parameters of both zeolite materials (synthetic and natural ZSM-5) and iron oxide impregnated derivatives are summarized in table 2. As it can be seen from figure 5b, all samples show an average pore diameter of ~1.93 nm and ~2.4 nm for synthetic ZSM-5 and Fe-impregnated synthetic ZSM-5, ~2.7 nm for natural ZSM-5 and Fe-impregnated ZSM-5, which means all samples exhibited a pore of micropore and mesopore, because it is within the range for microporous (d < 2 nm) and

| Material                  | Si  | Al  | Fe  | Si/Al Ratio |
|---------------------------|-----|-----|-----|-------------|
| Synthetic ZSM-5          | 28.73 | 0.62 | -   | 23.16       |
| Fe₂O₃/ZSM-5 Syn           | 33.33 | 1.17 | 1.23 | 14.24       |
| Natural ZSM-5             | 34.20 | 2.09 | -   | 8.18        |
| Fe₂O₃/ZSM-5 Nat           | 29.27 | 3.10 | 2.42 | 4.72        |

Figure 5. (a) N₂ isotherm adsorption curves, (b) Pore size distribution of synthetic ZSM-5, natural ZSM-5 and Fe-impregnated synthetic and natural ZSM-5.
Table 2. Textural parameters synthetic and natural ZSM-5 before and after impregnation.

| Material               | BET surface area [m²/g] | Total pore volume [cm³/g] |
|------------------------|--------------------------|----------------------------|
| Synthetic ZSM-5        | 281.418                  | 0.1751                     |
| Synthetic Fe₂O₃/ZSM-5  | 219.503                  | 0.1297                     |
| Natural ZSM-5          | 168.765                  | 0.0963                     |
| Natural Fe₂O₃/ZSM-5    | 165.875                  | 0.0947                     |

Figure 6. Percentage of methane conversion for all of the catalyst used.

mesoporous (d > 2 nm). On the other hand, natural ZSM-5 has a lower surface area than the synthetic ZSM-5, because as it can be seen from SEM image, natural ZSM-5 has a bigger morphology than synthetic ZSM-5, so its lower the surface area. Both impregnated synthetic and natural ZSM-5 showed lower surface area and pore volume than before impregnation, means the iron oxide has been successfully impregnated at the ZSM-5 surface.

3.3. Catalytic conversion of methane

The catalysts employed for the reaction were as-synthesized synthetic ZSM-5, as-synthesized natural ZSM-5, 1.23 % synthetic Fe₂O₃/ZSM-5 and 2.42 % natural Fe₂O₃/ZSM-5. Based on the experiment, it can be seen in figure 6 that both Fe-impregnated synthetic and natural ZSM-5 have higher percentage of methane conversion because the existence of iron oxide at the ZSM-5 surface makes it more reactive to break the H-CH₃ bond of the methane [18]. On the other hand, the higher percentage of methane conversion of 2.42 % natural Fe₂O₃/ZSM-5 than 1.23 % synthetic Fe/ZSM-5 could be explained by higher Fe-atomic percentage in natural Fe₂O₃/ZSM-5 (2.42 %) than synthetic Fe₂O₃/ZSM-5 (1.23 %).

The partial oxidation of methane in this experiment used O₂ as the oxidant (0.5 % O₂ in N₂ gas). The reaction was performed at 150 °C for 120 min. After the reactor was cooled down to room temperature, ethanol was injected to the reactor to extract the product from the catalyst then the products were analyzed using gas chromatography instrument with RTX-5 column and flame ionization detector.

The reaction results are shown in figure 7. It is shown that the reaction using natural ZSM-5 yielded formaldehyde whereas using synthetic ZSM-5 yielded formaldehyde and methanol. It is also shown the presence of Fe-oxide could not increase the percentage yield of formaldehyde. Both Fe-impregnated
Figure 7. Percentage yield of product of partial oxidation of methane reaction.

synthetic and natural ZSM-5 show a lower percentage yield of formaldehyde (39.973 % and 32.2 %) than non-impregnated synthetic and natural ZSM-5 (36.378 % and 42.325 %).

4. Conclusion
Hierarchical ZSM-5 has been successfully synthesized from Bayat natural zeolite and kaolin Bangka, and its properties are comparable to the as-synthesized synthetic ZSM-5. Both Fe-impregnated synthetic and natural ZSM-5 shows a higher percentage of methane conversion, but they give a lower percentage yield of formaldehyde than the parent as-synthesized ZSM-5 zeolites. So it could be concluded that the synthetic and natural ZSM-5 worked better in the partial oxidation of methane reaction.

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