Partial Oxidation of Methane Over NiOx/Hierachichal ZSM-5 Catalyst

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Partial Oxidation of Methane Over NiOx/Hierachichal ZSM-5 Catalyst

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Abstract. Methane is a primary component of natural gas that is considered a greenhouse gas. In this study, methane will be catalytically oxidized to methanol and its derivatives using hierarchical ZSM-5. The products are potential to be used as fine chemicals and additives in gasoline. The catalyst ZSM-5 (Si/Al = 35) was successfully synthesized by a double template method in which TPAOH is used as the MFI structure directing agent and PDDA-M is used as the secondary template. The as-synthesized hierarchical ZSM-5 was modified with metal oxide (M = Ni). Analysis with XRD indicates that ZSM-5 crystals have been formed with high crystallinity. SEM images showed hexagonal shape which is the characteristic of ZSM-5 crystals. Analysis with SAA indicated the presence of meso-sized pores by the presence of hysteresis loops. Surface area and pore volume have decreased after impregnation of Ni. Elemental analysis showed 2.73% nickel was loaded in the ZSM-5 framework. The catalytic reaction was carried out in batch reactor for 120 min. Two condition of gas feed was compared: CH₄: N₂ (without Oxygen) and CH₄: N₂-O₂ (with oxygen) with identical pressure ratio 0.75: 2 bar. Analysis by GC-FID showed that the catalytic activity of catalyst ZSM-5 with oxygen increase the methanol production.

Keywords: partial oxidation, ZSM-5 hierarchy, double template method, methane, methanol.

1. Introduction

The greenhouse effect is a UV light radiation event that should be reflected back outside the earth in the form of IR radiation, but is reabsorbed by an existing greenhouse gas in the atmosphere and then re-emitted to the earth, so that the UV equivalent energy is trapped on the surface earth. Methane is one of the greenhouse gas contributors. When the methane content in the atmosphere increased, it becomes an insulator that holds more heat from the sun that is emitted to the earth and hard to escape from the earth's surface.

Methane is the main component of natural gas. One of the most widely conducted studies is to convert methane through partial oxidation reactions with catalysts to methanol and other derivative products, thus having economic value and reducing methane gas emissions released into the atmosphere. Although methane can be used as fuel, the constraints are in the packaging and distribution of methane. This is because at room pressure and temperature, methane is a gas, while methanol is a liquid. Therefore, many researchers prefer to do a partial oxidation reaction converting methane to methanol to make it easier on the packaging process and produce environmentally friendly energy [1].
Hierarchical zeolite possesses two levels of porosity i.e microporous and mesoporous structures. This modification is based on the dissatisfaction of the catalytic properties of ZSM-5 microporous because it is considered to have poor mass transport properties, making it difficult for the reactants to enter into the zeolite pore [2]. This modification can be done with two approaches; top-down approach and bottom-up approach. Top-down approach is a modification process in pore by adjusting Si / Al ratio. There are two types of treatments for this approach: dealumination and desilication. Dealumination can be done by heating, while desilication can be done with the addition of a base. The addition of a base can make the tetrahedral SiO₄ bind and loose from the zeolite frame leaving the gap, but this method is destructive for the zeolite framework. Bottom-up approach is a process of pore modification by using soft or hard templates and cationic surfactants [2].

2. Materials and Methods

2.1 Materials

Tetraethyl orthosilicate (TEOS, 98%, Sigma Aldrich), Poly(Diallyldimethylammonium Chloride) (PDDA, 35%, Aldrich), NaAlO₂(Sigma Aldrich), tetrapropylammonium hydroxide (TPAOH, 1 M, Sigma Aldrich)), nickel(II) nitrate (Ni(NO₃)₂·6H₂O, 99.0% Merck), Ethanol (C₂H₅OH 99,9%), Methanol (CH₃OH 99,9%), formaldehyde (HCOH 37%), methane gas (99.99% UHP from BOC), N₂ gas (99.99 % UHP), O₂ gas (99.99% UHP) and deionized water.

2.2 NiOx/ZSM-5 Synthesis

Hierarchical ZSM-5 was synthesized by mixing 0.2964 g NaAlO₂, 36.7159 g TPAOH, 85.991 g H₂O, and 24.6069 g TEOSat 373 K for 3 h. 9,003 g PDDA (10%wt) was added into the mixture and stirred for 15 h at room temperature. Then, the mixture was placed in an autoclave and hydrothermally heated at 423 K for 144 h. The synthesized zeolite was dried at room temperature and followed by calcination at 823 K to remove the templates. Furthermore, Ni was impregnated into the zeolite by following method: 1 g of ZSM-5 was added to 1,7 mL larutan Ni(NO₃)₂ 0,2495 M and stirred for 24 h at room temperature followed by calcination at 823 K for 3 h. The synthesized zeolites were characterized by Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR, Shimadzu Prestige 21), Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDX), and Atomic Absorption Spectroscopy (Shimadzu AA 13000).

2.3 Catalytic Test

The synthesized catalyst was activated by calcination at 823 K for 3 h prior to be used in catalytic test. 0.5 g catalyst was placed in batch reactor and flushed by N₂ gas for 5 min. Different composition of gas feed was compared i.e CH₄-N₂ and CH₄-O₂-N₂ with pressure ratio 0.75: 2 bar. The catalytic reaction was performed at 423 K for 120 min. The product was separated by extraction using ethanol as solvent and then analyzed by gas chromatography (GC Shimadzu 2010) with a Carbowax column and flame ionization detector (Shimadzu).

3. Results

3.1 Catalyst characterization

ZSM-5 was synthesized by double template method in which TPAOH as MFI structure directing agent (mesoporous zeolites) and PDDA as mesoporous template. The XRD pattern of as synthesized ZSM-5 can be seen in Figure 1. There are two peaks between 2θ = 7-10° and three peaks between 2θ = 22-25°.This pattern shows typical peak of ZSM-5[3]. There are also peaks at 37.10 °, 44.40 °, 62.87 °, 76.50 °, and 79.22 ° which indicates the diffractogram patterns of nickel-shaped cubic. Ni addition to the structure of ZSM-5 decreases the peak intensity.It means that the crystallinity in ZSM-5 zeolite decrease after NiO modification. The metal oxide NiO also appeared at 44° [4].
Figure 1. XRD patterns of ZSM-5 (red), NiOx/ZSM-5 (blue), and nickel oxide (yellow)

Figure 2 shows the FTIR spectra of ZSM-5 before calcination (red) and after calcination (blue). The peaks at 1375-1450 cm$^{-1}$ (C-H stretching) and 2850-3000 cm$^{-1}$ (C-H bending) appeared in ZSM-5 before calcination but no peak observed at those wavenumber ranges in ZSM-5 after calcination. This indicates that both organic templates TPAOH and PDDA were removed from catalyst structure. The pores and channels of ZSM-5 were unoccupied after calcination.

The BET analysis shows that the average surface area of hierarchical ZSM-5 was 348.6 m$^2$/gr and after impregnated with NiOx was 330.3 m$^2$/gr. It can be seen in Figure 3a it can be seen that the catalyst shows H4 type hysteresis loop which indicates of mesoporous structure. In addition, the average pore diameter of catalyst was 1.8842 nm (micropore) and 2.741 nm which approximates the indication of pore formation with meso size (2 nm <d <50 nm).
Figure 3. (a) Isotherm adsorption-desorption, and (b) pore size distribution of as-synthesized hierarchical ZSM-5 and NiOx/ZSM-5

Figure 4. SEM images of ZSM-5. Left: 20.000x; Right: 50.000x

In Figure 4, it is clear that the ZSM-5 zeolite synthesized in this experiment has hexagonal geometry and appears to form coffin-like. However, the characteristic of mesoporous ZSM-5 which should look rough surface is unclear. EDX analysis showed the mole ratio of Si / Al was 34 in the first analysis. It is still within range of Si/Al ratio of initial target (32).

3.2 Catalytic test: partial oxidation of methane

The products were analyzed with Gas Chromatography (GC) using carbowax column. The highest yield of methanol 22.9 % was formed in the reaction using ZSM-5 in which O2 was added in gas feed whereas NiOx/ZSM-5 tends to form formic acid. This is a consequence of low crystallinity of zeolites which caused the dispersion of methane gas at the center of the activity is relatively unfavorable, this is crucial in the hydroxy formation stage. The low yield obtained in NiOx / ZSM-5 was influenced by oxygen-poor crystals (NiOx) in compared to metal with oxygen-rich crystals (CoOx) [5]. Furthermore, the presence of oxygen also affects the products yield.
4. Conclusions
The typical pores of hierarchical NiOx/ZrSM-5 (having both microporous and mesoporous) accelerate reactant diffusion into the catalyst pores. The low yield percentage with NiOx/ZSM-5 catalysts were assume because the lack of oxygen in nickel oxide crystal lattice, the molecular oxygen favour to undergo formic acid reaction mechanism.

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