Partial oxidation of methane to methanol over M.O./ZSM-5 (Mn, Fe, Co, and Ni) hierarchical transition metal oxide catalysts

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Abstract. The selective oxidation of methane to methanol is a key challenge in catalysis. The catalytic activities of nickel, cobalt, iron, and manganese oxides supported by hierarchical ZSM-5 zeolites for the partial oxidation of methane to methanol were studied. Hierarchical ZSM-5 was synthesized using a double-template method, in which tetrapropylammonium hydroxide was used as an MFI structure-directing agent and PDDA-M was used as a mesopore-directing agent. The synthesized hierarchical ZSM-5 was characterized by X-ray diffraction, Fourier-transform infrared spectroscopy, and scanning electron microscopy with energy dispersive spectroscopy. M/O/ZSM-5 catalysts were prepared using a wet impregnation method and were also extensively characterized. The catalytic test was performed at 423 K in a batch reactor with a CH4 to N2 ratio of 0.5:2 and 0.5 g of M/O/ZSM-5 catalyst for 2 h. The hierarchical Fe2O3/ZSM-5 catalyst showed the highest yield of methanol, whereas Mn3O4/ZSM-5 tended to produce formic acid.

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

1. Introduction

Natural gas has been known as a clean and effective energy source since its combustion generates fewer greenhouse gases than coal or petroleum fuels. However, its storage and transport is not easy, making its derivatives uncompetitive with those of other fossil fuels [1]. Conventionally, an indirect route for conversion of natural gas to methanol was through the production of syngas. However, the process is an energy intensive process, (temperature reaction of 800 °C–1000 °C) and more than 25 % of the feed (natural gas) has to be burned to provide the heat of reaction [2]. Hence, such a sustainable direct conversion of methane to methanol is more desirable compared with the current technology [3].

Research into the direct partial oxidation of methane has progressed rapidly, and several developments have been made, including the use of oxidants such as N2O, O2, and H2O2. The catalysts used are metal oxides such as CoO and MoO3 in conjunction with zeolites and some transition metals as active sites, such as Fe, Co, and Cu. Nadzeya et al. [4] carried out partial oxidation of methane using a Co-impregnated agglomerate of ZSM-5 zeolite as a catalyst and obtained methanol and formaldehyde as the major products. Furthermore, Krisnandi et al. [5] used a hierarchical CoO/ZSM-5 catalyst, and the reaction showed a high selectivity toward methanol conversion [5]. In this work, we compared the activities of four hierarchical ZSM-5 supported catalysts based on metal oxides MnO, FeO, NiO, and CoO, for partial oxidation of methane.

2. Experimental

2.1. Materials
All materials in this work were used without further purification. Tetraethyl orthosilicate (TEOS, 98%, Sigma Aldrich), sodium aluminate (Sigma Aldrich), poly(diallyldimethylammonium chloride) (PDDA, 35%, Aldrich), and deionized water were used for hierarchical ZSM-5 synthesis. While cobalt(II) nitrate (Co(NO$_3$)$_2$·6H$_2$O, Sigma Aldrich), iron(III) nitrate (Fe(NO$_3$)$_3$·9H$_2$O, Sigma Aldrich), manganese (II) nitrate (Mn(NO$_3$)$_2$·4H$_2$O, Sigma Aldrich), nickel(II) nitrate (Ni(NO$_3$)$_2$·6H$_2$O, Sigma Aldrich) were used to prepare M.O./ZSM-5. Finally, methane gas (99.99% BOC), N$_2$ gas (99.99% UHP) were used in catalytic test.

2.2. ZSM-5 synthesis and M.O./ZSM-5 preparation

The synthesis was carried out following method reported by Wang et al. [6] with some modifications. Hierarchical ZSM-5 was synthesized by mixing the solution of sodium aluminate, TEOS, TPAOH and deionized water in a molar ratio of 1 [Al$_2$O$_3$] : 64 [SiO$_2$] : 10 ([TPA]$_2$O) : 3571 [H$_2$O] at 373 K for 3 h. Afterward, this mixture was added dropwise by 1 g PDDA stirred for 24 h, then hydrothermal processed in a Teflon-lined stainless steel autoclave at 423 K for 144 h. The then obtained zeolite (white powder) was dried in room temperature before calcined at 820 K. Metal oxide insertion into the zeolite was carried out using a wet impregnation method, where 1 g of ZSM-5 was added to 0.2495 M metal solution prepared from metal nitrate hydrate and stirred for 24 h at ambient condition, followed by calcination at 823 K. Respectively, the hierarchical ZSM-5 and M.O.-ZSM-5 counterparts were characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR, Shimadzu Prestige 21), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDX, SEM FEI quanta FEG 450), and atomic absorption spectroscopy (AAS, Shimadzu 13000).

2.3. Catalytic test: partial oxidation of methane

The methane partial oxidations were performed using each M.O./ZSM-5 catalysts (c.a. 0.5 g) in a 200 mL stainless steel batch reactor. Prior to use, the catalyst (0.5 g) was activated at 773 K and flushed with flowing nitrogen gas. The catalytic reaction was carried out at 423 K for methane and nitrogen pressures of 0.75 and 2 bar, respectively. After the reactor was left to cool down to room temperature, reaction product was extracted from the zeolite using 3 mL of ethanol and analyzed using gas chromatography (GC Shimadzu 2010) with a Carbowax column and flame ionization detector (Shimadzu).

3. Results and discussion

3.1. Characterization of ZSM-5

3.1.1. XRD Pattern. The ZSM-5 zeolite was synthesized using TPAOH as an MFI structure-directing agent and PDDA polycation as a mesopore template. During the formation of zeolites with Si/Al ratios ranging from 10.5 to 36.5, competition between ZSM-5 and mordenite occurred during the hydrothermal crystallization process [5]. However, the positively charged PDDA interacts with the negatively charged ZSM-5 crystal-to-be-structure, so that the ZSM-5 framework could be established around the PDDA polycation [6]. The XRD pattern of as-synthesized hierarchical ZSM-5 (figure 1) shows certain peaks in the 20 range from 7° to 9° and from 22° to 25°, which is consistent with the standard ZSM-5 pattern [7], indicating that the ZSM-5 structure was successfully synthesized [6].

3.1.2. FTIR Spectroscopy. Figure 2 shows the FTIR spectra of ZSM-5 before (a) and after (b) calcination. The spectrum of ZSM-5 before calcination shows several extra peaks at 2900–2850 cm$^{-1}$ (C–H stretching) and at 1470–1350 cm$^{-1}$ (C–H bending) compared with that of ZSM-5 after calcination, which can be attributed to the templates used in the synthesis of zeolite, i.e., TPAOH and PDDA. Calcination was performed to remove the organic templates used in the synthesis of zeolites. It can be seen from figure 2b that the template was removed as indicated by the loss of the C–H stretching and bending vibration bands. Moreover, the pores and channels in the zeolite became unoccupied after calcination.

3.1.3 SEM-EDX. To determine the crystal structure and the Si/Al ratio of the synthesized zeolite, EDX analysis was performed, from which the mass% of the elements in the zeolite can be determined, in which the Si/Al ratio was 37.4. Table 1 shows the mass% of the elements present in a ZSM-5 crystal.
Figure 1. XRD patterns of (a) synthesized ZSM-5 and (b) standard ZSM-5.

Table 1. SEM-EDX analysis

| Element | Composition |
|---------|-------------|
| C       | 1.17        |
| O       | 50.04       |
| Na      | 0.41        |
| Si      | 46.42       |
| Al      | 1.24        |

Figure 2. FTIR Spectra ZSM-5 (a) before and (b) after calcination at 823 K.

3.2. Preparation of M.O/ZSM-5

M.O/ZSM-5 heterogeneous catalysts were prepared using a wet impregnation method. The elemental analysis with AAD indicates that the loading of each metal on ZSM-5 zeolites was about 2.1%–2.5%.

Figure 3 shows the XRD patterns of modified ZSM-5 catalysts. The peaks at $2\theta = 31^\circ$, $47^\circ$, and $58^\circ$ in the diffraction pattern of NiO/ZSM-5 are attributed to NiO [8]. The peaks at $2\theta = 31^\circ$, $44^\circ$, and $45^\circ$ in the diffraction pattern of FeO/ZSM-5 originates from FeO [9]. Moreover, the peaks at $2\theta = 31^\circ$, $45^\circ$, $55^\circ$, and $60^\circ$ in the diffraction pattern of CoO/ZSM-5 are attributed to CoO [10], and the peaks at $2\theta = 35^\circ$ and $40^\circ$ are attributed to CoO [11]. The peaks at $2\theta = 19^\circ$ and $25^\circ$ in the diffraction pattern of MnO/ZSM-5 originate from MnO, and the peaks at $2\theta = 16^\circ$, $31^\circ$, and $65^\circ$ originate from MnO [12].
Figure 3. XRD patterns of (a) NiO/ZSM-5, (b) FeO/ZSM-5, (c) MnO/ZSM-5, and (d) CoO/ZSM-5.

Figure 4. Results of partial oxidation of methane using unmodified ZSM-5 and metal oxide-modified ZSM-5.

3.3. Methane partial oxidation catalytic test

The results of methane partial oxidation using as synthesized ZSM-5 catalysts are shown in figure 4. ZSM-5 without metal oxides produced methanol in 6.8% yield. The impregnation of most metal oxides in ZSM-5 increased the % yield of methanol, which indicates that the metal oxide is capable of being the active site of the catalyst, thereby increasing the catalytic activity for oxidizing methane to
methanol. However, when using MnO$_3$-modified ZSM-5, formic acid was formed with higher yield than methanol, indicating MnO/ZSM-5 has selectivity toward the formation of formic acid.

4. Conclusions
Catalysts based on ZSM-5 modified with four metal oxides have been successfully synthesized, as confirmed by XRD data. The presence of metal oxides increased the number of catalyst active sites, resulting in high yield of methanol. It was found that the type of metal oxide species influenced the yield of methanol. Among the four types of metal oxide-modified ZSM-5 catalysts, Fe$_2$O$_3$/ZSM-5 is the most promising for partial oxidation of methane to methanol with the highest yield of 30.5%, whereas MnO/ZSM-5 has selectivity toward the formation of formic acid.

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