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## Partial Oxidation of Methane to Methanol over Heterogeneous Catalyst Co/ZSM-5

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### Abstract

The catalytic activities of four types of Co/ZSM-5 zeolites in partial oxidation of methane were compared to observe the effect of pore size and cobalt species to the reaction. Two types of ZSM-5 structures: microporous and hierarchical; and two ways of Co loading: impregnation and ion exchange were studied. The catalytic test was performed at 423 K in a batch reactor (volume c.a. 200 cm<sup>3</sup>) with methane to N<sub>2</sub> ratio of 0.5:2, and 0.5 g Co/ZSM-5 catalyst. The results show that the partial oxidation of methane was selective to methanol production for all four ZSM-5 zeolites. The hierarchical Co/ZSM-5 showed to give the highest conversion of methane to methanol.

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**Keywords:** Co-ZSM-5; hierarchical zeolite; methane; methanol; partial oxidation

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**Nomenclature**

<b>ZSM-5</b>	Zocony Structure Mobil Oil-5	<b>H_ZSM-5</b>	Hierarchical ZSM-5
<b>TPAOH</b>	Tetra Propyl Ammonium Hydroxide	<b>Mi Co/ZSM-5</b>	Cobalt-impregnated Microporous ZSM-5
<b>PDDA</b>	Poly Diallyl Dimethyl Ammonium Chloride	<b>Hi Co/ZSM-5</b>	Cobalt-impregnated Hierarchical ZSM-5
<b>M_ZSM-5</b>	Microporous ZSM-5	<b>Hie Co/ZSM-5</b>	Cobalt-ion exchanged Hierarchical ZSM-5

**1. Introduction**

Biogas is a mixture of methane ( $\text{CH}_4$ ) and carbon dioxide ( $\text{CO}_2$ ) along with other trace gases, generated in landfills as waste decomposes, and in the treatment of wastewater. Methane's lifetime in the atmosphere is much shorter than  $\text{CO}_2$ , but  $\text{CH}_4$  is more efficient at trapping radiation than  $\text{CO}_2$ . Therefore, the comparative impact of  $\text{CH}_4$  on climate change is over 20 times greater than  $\text{CO}_2$  over a 100-year period. Due to being the part of greenhouse gases, it is desirable to convert methane into liquid transportable fuels such as methanol because it retains most of methane energy and produce clean environment<sup>1</sup>.

Recently, in order to utilize methane, partial oxidation reaction becomes one of main research interests<sup>2-5</sup>. Research in methane conversion to methanol and formaldehyde through partial oxidation using Co-impregnated agglomerate of ZSM-5 zeolite as heterogeneous catalyst at 423 K has been reported<sup>6</sup>. In that work, the agglomeration has caused hierarchical pores within the zeolite, while methanol and formaldehyde are observed as the main products.

Hierarchical porosity in the zeolite has been introduced using various synthesis and modification methods<sup>7-11</sup>. Some methods employed polymer cationic as secondary template to create mesoporosity, in addition to the common quaternary ammonium cation as the micropore template<sup>11</sup>. In this research mesoporous ZSM-5 was synthesized hydrothermally using Poly Diallyl Dimethyl Ammonium (PDDA) as mesopore template. The focus of this work is to observe the influence of variation methods of cobalt insertion to mesoporous ZSM-5 on their catalytic performance in partial oxidation of methane. In addition, the results have also shown the role of mesoporosity in the ZSM-5 zeolite in the methane conversion and the methanol yield.

**2. Material and methods***2.1. Material*

All materials are used as received without further purification. Tetraethylorthosilicate (TEOS) 98 % (Aldrich), Sodium Aluminate (Sigma Aldrich), Tetrapropylammonium hydroxide, TPAOH 1M (Sigma Aldrich), Poly Diallyl Dimethyl Ammonium Chloride (PDDA 35 %) (Aldrich), Cobalt (II) Nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) (Sigma Aldrich), methane gas (99.99 % BOC),  $\text{N}_2$  gas (99.99 % UHP) and deionized water.

*2.2. ZSM-5 synthesis and Co-ZSM-5 preparation*

- Hierarchical ZSM-5 was synthesized by mixing sodium aluminate solution TPAOH and TEOS with molar ratio of  $1 \text{ Al}_2\text{O}_3 : 64 \text{ SiO}_2 : 10 (\text{TPA})_2\text{O} : 3571 \text{ H}_2\text{O}$  at 373 K for 3 h. About 1 g PDDA was added slowly to the mixture at room temperature and stirred for 24 h. Then, mixture was placed in autoclave for hydrothermal process at 423 K for 144 h. Afterward, the as-synthesized zeolite was dried at room temperature followed by calcination at 823 K.
- Microporous ZSM-5 was synthesized in similar manner, but without the addition of PDDA polycation as secondary template.
- Cobalt insertion to the zeolite was carried out using two different methods: wet impregnation method and ion-exchange technique. In wet impregnation method, 1 g of ZSM-5 was added to 0.249 5 M cobalt(II) solution prepared from  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and stirred for 24 h in room temperature then calcined at 823 K. Multiple Co-

exchange method was employed by dispersing 1g ZSM-5 to 0.1 M Cobalt(II) solution followed by calcination at 573 K.

- The ZSM-5 and Co-ZSM-5 zeolites were characterized using FT-IR (Shimadzu IR Prestige 21), XRD (Axios PanAnalytical), Pore size Analyzer (Quantachrome Quadrawin v3.21 and ASAP 2400), FE-SEM-EDX, and Atomic Absorption Spectroscopy (AA 6300), and TEM.

### 2.3. Catalytic Test – partial oxidation of methane

The catalytic tests, partial oxidation of methane using each Co/ZSM-5 catalyst, were conducted in stainless steel vessel as a batch reactor. The catalyst used for each reaction was c.a. 0.5 g, in which was activated at 773 K and flushed by nitrogen gas prior being used. The reaction was done at 423 K with variations of methane:nitrogen pressure of 0.5 : 2, 0.75 : 2, and 1 : 2 (in kPa), giving the  $P_{\text{methane}}$  of 25.33 kPa, 38.00 kPa, and 50.66 kPa respectively. The product from this reaction then was extracted from Co/ZSM-5 with ethanol to be characterized using Gas-Chromatography Flame Ionization Detector (Shimadzu 2010). Catalytic test was also carried out using H\_ZSM-5 as catalyst as control.

## 3. Result and discussion

### 3.1. Characterization of ZSM-5 zeolites

#### 3.1.1. XRD pattern

The ZSM-5 zeolites were synthesized using TPAOH as the micropore template and structure-directing agent for MFI-type zeolite, whereas in order to create mesoporosity within the structure, PDDA polycation was added. Soft templates such as PDDA have two possible positions in the zeolite, during the crystallization process, in which it could coat on the inside and outside of the zeolite particles. In the formation of zeolites with Si/Al ratio from 10.5 to 32.5, during hydrothermal zeolite crystallization process, the competition between ZSM-5 and Mordenite occurred. Positively charged PDDA interacts with the negatively charged structure of zeolite which is an advantage compared to the hard template<sup>11</sup>. Diffraction patterns of microporous and mesoporous ZSM-5 (labeled as M\_ZSM-5 and H\_ZSM-5, respectively) showed the appearance of certain peaks in the position 2 theta between 7° to 9° and 22° to 25° (Figure 1), indicative of successfully synthesized ZSM-5 structure.

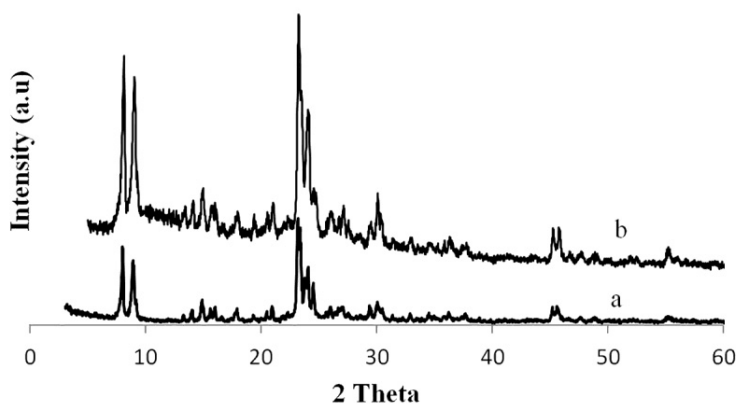


Figure 1. XRD patterns of a. microporous and b. hierarchical ZSM-5

### 3.1.2. Surface area analysis

The results of surface area analyses from four types of ZSM-5 are summarized in Table 1. It can be seen that the surface area of hierarchical ZSM-5 is larger than the microporous counterpart. This is supported by the isotherm adsorption-desorption plots of both ZSM-5 materials shown in Figure 2. The hysteresis loop at 0.5 to 0.9 P/P<sub>0</sub>, indicative of mesoporous character, is observed in the isotherm desorption of the hierarchical ZSM-5 (H\_ZSM-5), but not in that of microporous M\_ZSM-5. The pore volume of H\_ZSM-5 is also larger than that of M\_ZSM-5.

Table 1. Surface area analyses of ZSM-5 catalysts calculated from BET measurement

Analysis	M_ZSM-5	H_ZSM-5	Mi_Co/ZSM-5	Hi_Co/ZSM-5	Hie_Co/ZSM-5
BET Surface area (m <sup>2</sup> · g <sup>-1</sup> )	416.17	435.0	373.08	398.01	264.8
Average pore diameter (nm)	1.84	7.36	1.97	8.17	3.95
Pore volume (cc · g <sup>-1</sup> )	0.26	0.84	0.25	0.81	0.42

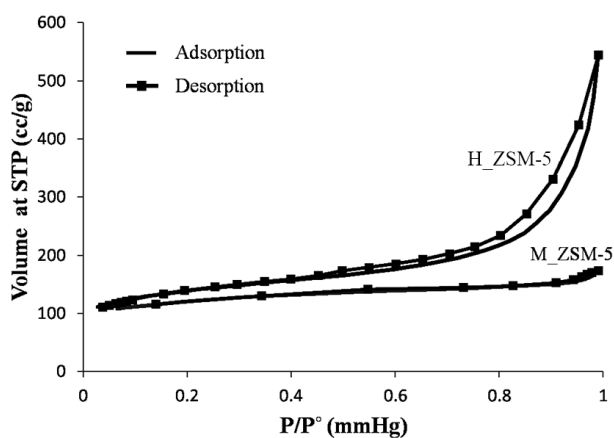


Figure 2. Isotherm adsorption-desorption plots of M\_ZSM-5 and H\_ZSM-5

### 3.1.3. SEM-EDX

Figure 3 shows the images of M\_ZSM-5 and H\_ZSM-5. Both zeolites have crystal shape of coffin-like which is typical shape of ZSM-5. The morphology of M\_ZSM-5 surface (Figure 3a) somehow is smoother than the surface of H\_ZSM-5 (Figure 3b). The rough surface is caused by the mesoporosity created after the secondary template was removed after calcination at 823 K. This result was also reported by Wang et al<sup>11</sup>.

### 3.2. Preparation of Co/ZSM-5 zeolites

The Co/ZSM-5 heterogeneous catalysts were prepared using two different methods, wet impregnation Co-impregnated micro-and hierarchical ZSM-5 (labeled as Mi\_ZSM-5 and Hi\_ZSM-5, respectively) and ion exchange methods Co-exchanged hierarchical ZSM-5 (labeled as Hie\_ZSM-5). Elemental analysis measurement using AAS (Table 2) shows that the cobalt loaded into the ZSM-5 zeolites are 2.36 wt%, 2.28 wt% and 2.12 wt% respectively for Mi\_Co/ZSM-5, Hi\_Co/ZSM-5 and Hie\_Co/ZSM-5.

Table 2. %Co Loading of Co/ZSM-5 calculated from AAS measurement

Catalysts	Co (wt%)
Mi_Co/ZSM-5	2.355%
Hi_Co/ZSM-5	2.418%
Hie_Co/ZSM-5	1.447%

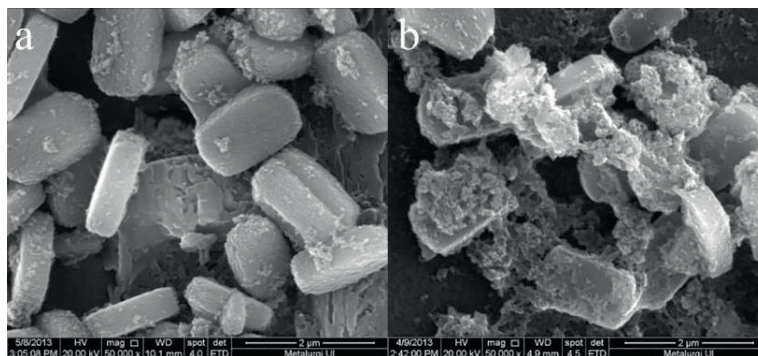


Figure 3. Electron Microscope images of (a) M\_ZSM-5 and (b) H\_ZSM-5(at 50000 ×)

The surface area analysis for Co/ZSM-5 catalysts (Table 1) showed that a decrease in surface area and total pore volume of the all Co/ZSM-5 catalysts compared to the ZSM-5 parents. This proves that the cobalt species has penetrated into the pores and surface of ZSM-5 structure.

The XRD patterns in Figure 4 showed that the patterns of Mi\_ZSM-5 and Hi\_ZSM-5 and Co-exchanged hierarchical ZSM-5 are quite similar to that of ZSM-5 parents. This suggested that the addition of Co species either by ion exchange or impregnation method did not cause structural damage of ZSM-5. However, the background signals of micro and hierarchical Co-ZSM-5 is higher than the parent ZSM-5, indicating that the crystallinity of the catalysts was decreased due to the interaction between cobalt oxide species with ZSM-5 structure. Additionally, there are new weak peaks in the 2-theta of 21°, 32°, 36° and 48° which could be attributed to Co<sub>3</sub>O<sub>4</sub> species and 29°, 42°, 57° could be assigned for Co<sub>2</sub>SiO<sub>4</sub> species<sup>16</sup>. This is an evidence of the presence of cobalt oxide species in the ZSM-5 catalysts.

### 3.3. Catalytic test: methane partial oxidation

Prior to the catalytic reaction, the ZSM-5 catalyst must be first activated at a temperature of 823 K with the aim to form cobalt oxide species which constitute the active site of the catalyst Co/ZSM-5. Furthermore, flushing was carried out using nitrogen gas to remove organic impurities, water vapour and excess oxygen in the reactor. The condition of the reaction was adapted from the work reported by Bezniz et.al<sup>6</sup>. The first set of experiments was carried out at 423 K with reaction time of 30 min and 60 min, and variation of CH<sub>4</sub> pressure ( $P_{\text{methane}}$ ) of 25.33 kPa, 38.00 kPa and 50.66 kPa in 200 cm<sup>3</sup> stainless steel vessel. The results of this experiment are summarized in Figure 5a. It can be seen that for all three cobalt-loaded ZSM-5, the highest conversion of methane to methanol was obtained when the composition of methane to nitrogen in the vessel is 0.75:2 kPa or the partial pressure of methane ( $P_{\text{methane}}$  of 38.00). The cobalt-loaded hierarchical ZSM-5 catalysts gave higher conversion than the microporous Mi\_Co/ZSM-5. This is indicative of the influence of pore-size for the partial oxidation of methane to take place. Furthermore, the highest % conversion is observed when Hie\_Co/ZSM-5, prepared through ion exchange method, was in use. It is suggested that Co-species occupied most of the position of Na<sup>+</sup> ions during ion exchange treatment and some of them became active sites after calcination. When the reaction took place for 60 min, as shown in Figure 5b, the highest conversion of methane to methanol was resulted in from the reaction catalysed by Hi\_Co/ZSM-5 (42 %), followed by Mi\_Co/ZSM-5 (16 %), then Hie\_Co/ZSM-5 (7.56 %) and H\_ZSM-5 (8.4 %).

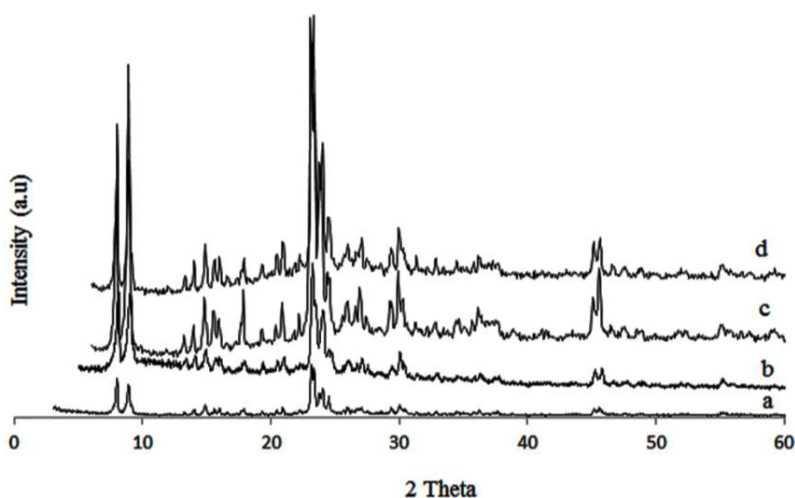


Figure 4. The XRD patterns of (a) M\_ZSM-5, (b) H\_ZSM-5, (c) Mi\_Co/ZSM-5 and (d) Hi\_Co/ZSM-5

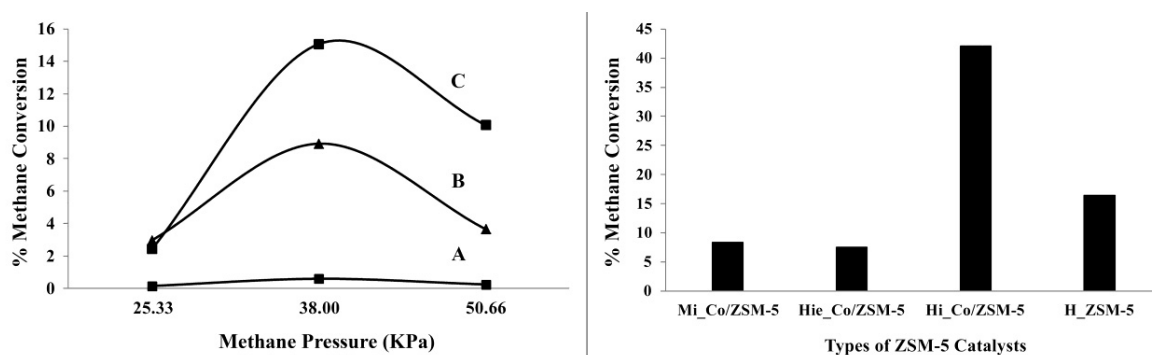


Figure 5 Catalytic test: (a) Optimum partial pressure of methane using A. M<sub>Co</sub>/ZSM-5, B. Hi<sub>Co</sub>/ZSM-5, and C. Hie<sub>Co</sub>/ZSM-5 (reaction Condition: T=423 K, t=30 min); and (b) % methane conversion to methanol from reaction carried out at 423 K, t=60 min and methane partial pressure of 38 kPa.

Methane gas is a very stable compound. In this conversion, activating CH bonds in methane was considered as the decisive step in the catalytic reaction both theoretically and experimentally<sup>6,16</sup>. From the results obtained it can be seen that the optimal catalytic reaction occurs at a time of 60 min with CH<sub>4</sub>:N<sub>2</sub> introduced at P<sub>methane</sub> of 38.00 kPa using Co-impregnated hierarchical (Hi<sub>Co</sub>/ZSM-5) as catalyst. The use of microporous Mi<sub>Co</sub>-ZSM-5 catalyst gives smaller conversion (16 %). This is because the pore size of the Mi<sub>Co</sub>/ZSM-5 is very small so that the substrate mass transport process is very difficult. On the other hand, when hierarchical cobalt-loaded via ion-exchange, Hie<sub>Co</sub>/ZSM-5, was used, the conversion of 7.56 % was obtained. This is because the use of the wet impregnation method of Co(NO<sub>3</sub>)<sub>2</sub> followed by calcination at 823 K has created cobalt oxides that active as catalyst.

While, the cobalt loading via ion-exchange method followed by calcination at 573 K seemed not yet completely change the cobalt (II) ions to its oxides due to the fact that they have to balance the ZSM-5 structure that inherently has negative formal charge. So that the amount of cobalt oxides present as active catalyst was less than required.

### 3.4. Catalyst regeneration

It can be seen from the catalytic test that the conversion from cobalt (II) ions to cobalt-oxide species is important, as well as the amount of the active cobalt-oxide species during the catalytic reaction. This is supported by the work of Bezniz et al.<sup>6</sup> and Fellah and Onal<sup>16</sup>. TEM measurement (Figure 6) of the fresh Hi\_Co/ZSM-5 and after used and calcined at 823 K indicates that the profile of the catalyst is not damaged after used and regenerated. Currently, serials of experiments are carried out to test the performance of the catalyst after multiple use and regeneration.

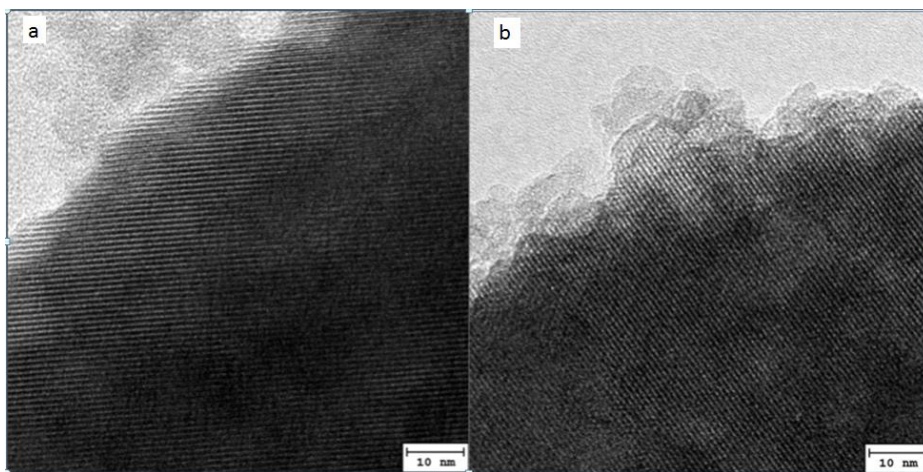


Figure 6. TEM images of Hi\_Co/ZSM-5: (a) fresh and (b) after used and regenerated

## 4. Conclusion

Three types of Co/ZSM-5 zeolite catalysts have been prepared and their catalytic activities were tested in the partial oxidation of methane to methanol. It is shown that both mesoporous properties and type of Co-species play important role in the use of the Co/ZSM-5 as heterogeneous catalyst in this reaction. Larger pore size of ZSM-5 resulted in higher % conversion as it provides more space for Co-loading and the catalyst conversion to take place. The types of Co-species influence the % conversion of methane, in which in this work, impregnation method creates more active Co-oxide compound than ion-exchange method. Finally, the hierarchical Co/ZSM-5 is promising to be used as the catalyst for partial oxidation of methane to methanol.

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