

Carbon monoxide methanation over Nickel promoted HZSM-5 (Ni/HZSM-5)

Teh Lee Peng^{1*}, Herma Dina Setiabudi^{2,3} and Aishah Abdul Jalil^{4,5}

¹ Department of Chemical Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia.

² Faculty of Chemical and Process Engineering Technology, College of Engineering Technology, Universiti Malaysia Pahang, 26300 Gambang, Kuantan, Pahang, Malaysia.

³ Centre of Excellence for Advanced Research in Fluid Flow, Universiti Malaysia Pahang, 26300 Gambang, Kuantan, Pahang, Malaysia.

⁴ Department of Chemical Engineering, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia.

⁵ Centre of Hydrogen Energy, Institute of Future Energy, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia.

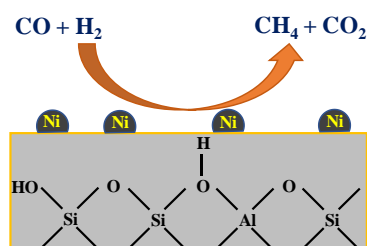
*Corresponding Author: lpteh@ukm.edu.my

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GRAPHICAL ABSTRACT



ABSTRACT

The CO methanation was studied over 5wt% Ni loaded on HZSM-5 (5Ni/HZSM-5) catalyst via conventional impregnation technique. The catalyst's characterization was based on X-ray diffraction (XRD), N₂ physisorption, and FTIR adsorbed pyrrole analysis. Catalytic activity of CO methanation was conducted at 150-450 °C. The XRD analysis illustrated that the modification of 5wt% of Ni metal onto HZSM-5 support did not significantly alter the crystallinity compared to that of unmodified HZSM-5. The N₂ physisorption result showed the co-existence of micro-mesoporosity in 5Ni/HZSM-5. The FTIR adsorbed pyrrole analysis demonstrated that 5Ni/HZSM-5 possessed high number of basic sites. The 5Ni/HZSM-5 exhibited low-temperature catalytic performance at 350 °C with 100% of CO conversion and 96.4% of CH₄ yield. The CH₄ yield increased to 99.6% at 450 °C with only negligible amount of CO₂ was observed. The good performance in CO methanation over 5Ni/HZSM-5 can be related to the presence of Ni metal, presence of micro-mesoporosity and high basicity of the material.

Keywords: CO methanation, Ni metal, HZSM-5, micro-mesoporosity, basicity

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1. INTRODUCTION

Catalytic methanation of carbon monoxide is an effective process for the purification of hydrogen-rich gas reformates by means of CO removal for fuel cell application. To prevent degrading the electrochemical efficiency of Pt anode due to CO-poisoning, there is a need for low CO concentration level (<10 ppm) in the conventional fuel cells [1]. Thermodynamically, CO methanation is a highly exothermic process. The catalytic activity of CO methanation may be affected by several undesirable secondary processes such as CO₂ methanation and reverse water gas shift (RWGS). The CO methanation is presented by Equation (1) [2]. Therefore, the discovery of new catalysts with high CO methanation activity to solve the problem is needed.



In this case, Ru, Rh and Pt noble metal supported catalysts have been successfully developed and considered extremely efficient in the CO methanation reaction. However, the low availability and high costs have limited

their industrial applications [3]. Therefore, other approaches have been attempted with the use of Ni non-noble metal-supported catalysts.

Different supporting materials for Ni-based catalysts have been explored in several studies. Italiano et al. [4] stated that the Ni-support interactions is important for high activity in low temperature CO and CO₂ methanation. Another study by Liu et al. [5] also stated that medium Ni-support interaction and highly dispersed small diameter of Ni particles on the support would be the reasons for good activity in CO methanation.

The present study concentrates on the preparation, characterizations, and catalytic CO methanation testing on 5Ni/HZSM-5. It is found that 5Ni/HZSM-5 catalyst could be a promising material towards low temperature catalytic methanation of CO.

2. EXPERIMENTS

2.1 Preparation of Catalyst

A commercial HZSM5 support (Si/Al = 50, Zeolyst International) was utilized. The wet impregnation method using aqueous nickel nitrate (Ni(NO₃)₂•6H₂O) was

employed to prepare 5 wt% Ni-promoted HZSM-5(50) at 80 °C. The sample was undergone overnight drying at 110 °C and air calcination at 550 °C for 3 hours.

2.2. Characterization

The catalyst's crystalline structure was examined using Bruker Advance D8 X-ray powder diffractometer with a Cu K α radiation source (40 kV, 40 mA) in the range of $2\theta = 2-90^\circ$. The Beckman Coulter SA3100 instrument has been used to determine the catalyst's nitrogen physisorption properties (surface area, total pore volume and pore size distribution). The catalyst was outgassed for 1 hour at 300 °C before proceed to N₂ adsorption measurement at -196 °C. The measurement of basicity was conducted on a FTIR spectrometer (Agilent Cary 640) with adsorption of 4 Torr pyrrole on activated samples at room temperature for 5 minutes, accompanied by outgassed at room temperature, 50, 100, 150, and 200 °C for 5 minutes. Before pyrrole adsorption analysis, pre-activation of all samples was carried out at 400 °C for 1 hour.

2.3 Catalytic Testing

The methanation of carbon monoxide was performed in a fixed-bed quartz microcatalytic reactor at 150-450 °C. For measurement of the actual pretreatment and reaction temperatures, the thermocouple was inserted directly into the bed of catalyst. Initially, 0.2 g of catalyst was pretreated for 1 hour in an oxygen stream ($F_{Oxygen} = 100$ ml/min) followed by 3 hours at 500 °C in a hydrogen stream ($F_{Hydrogen} = 100$ ml/min) and cooled down in a hydrogen stream to the desired reaction temperature. When the reactor temperature became stable, a reactant mixture consisting of H₂ and CO was fed into the reactor at a particular gas hourly space velocity (GHSV) and mass ratio of H₂/CO. An on-line 6090N Agilent gas chromatograph fitted with a TCD detector was used to analyze the composition of the outlet gases. The carbon monoxide conversion and the product selectivity (CH₄ and CO₂) were determined using the following equations:

$$X_{CO} (\%) = \frac{M_{CH_4} + M_{CO_2}}{M_{CO} + M_{CH_4} + M_{CO_2}} \times 100 \quad (2)$$

$$S_{CH_4} (\%) = \frac{M_{CH_4}}{M_{CH_4} + M_{CO_2}} \times 100 \quad (3)$$

$$S_{CO_2} (\%) = \frac{M_{CO_2}}{M_{CH_4} + M_{CO_2}} \times 100 \quad (4)$$

$$Y_{CH_4} (\%) = \frac{X_{CO} \times S_{CH_4}}{100} \quad (5)$$

$$Y_{CO_2} (\%) = \frac{X_{CO} \times S_{CO_2}}{100} \quad (6)$$

where X_{CO} is the conversion of carbon monoxide (%), S_{CH_4} and S_{CO_2} is the selectivity of CH₄ (%) and CO₂ (%), respectively, Y_{CH_4} and Y_{CO_2} is the yield of CH₄(%) and CO₂(%), respectively; M is a mole of the CO, CH₄ or CO₂.

3. RESULTS AND DISCUSSION

Fig. 1 shows the patterns of XRD for HZSM-5 and 5Ni/HZSM-5 catalysts. The patterns exhibited several peaks at $2\theta = 7-10^\circ$ and $22-25^\circ$ (JCPDS 42-0024), which are reflections of the typical characteristic pattern of MFI type ZSM-5 zeolite [6,7]. Besides, both catalysts demonstrated high crystallinity.

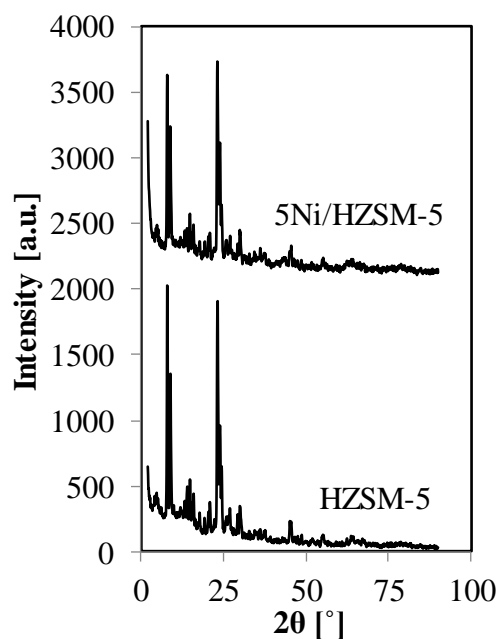


Fig. 1 XRD patterns of the samples.

However, after the introduction of Ni, the intensity of HZSM-5 was slightly diminished. In wide-angle XRD ($2\theta = 30-90^\circ$), there is absence of the peaks of NiO metal crystallites, indicating highly dispersion of NiO particles and/or small crystallite size of NiO, which is lower than the XRD detection limit. Moreover, Czuma et al. [8] reported the study of CO₂ methanation with Ni/zeolite X originated from fly ash. The authors stated that smaller amount of nickel loading will have higher metal-support interaction and smaller crystallite size as comparison to the higher loading of nickel which contributed to weak metal-support interaction and larger crystallite size. Fig. 2 displays the HZSM-5 zeolite catalyst structure.

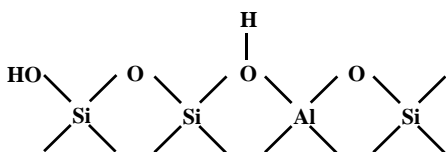


Fig. 2 Structure of the HZSM-5 zeolite

The textural properties of the 5Ni/HZSM-5 was summarized in Table 1. The 5Ni/HZSM-5 catalyst possessed surface area of 375 m²/g, total pore volume of 0.2810 cm³/g and average pore size of 2.99 nm.

Table 1 Textural properties of the 5Ni/HZSM-5

Catalyst	Surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore size (nm)
HZSM-5*	406	0.2540	-
5Ni/HZSM-5	375	0.2810	2.99

*Obtained from Kolobova et al. [9]

Fig. 3(A) and (B) displays the nitrogen adsorption-desorption isotherm and pore size distribution of 5Ni/HZSM-5 catalyst, respectively. According to the IUPAC classification, the 5Ni/HZSM-5 catalyst exhibited an isotherm of type I and an intense rise at low relative pressure confirmed the characteristic micropore framework with relatively small external surface. Whereas, typical hysteresis loop of microporous material obviously shows differently in 5Ni/HZSM-5 catalyst by appearing a type H4 hysteresis loop, attributable to pores with narrow slit and presence of mesoporosity. This phenomenon is usually found in micro-mesoporous material [10,11]. Moreover, the presence of mesopores was possibly due to an apparent

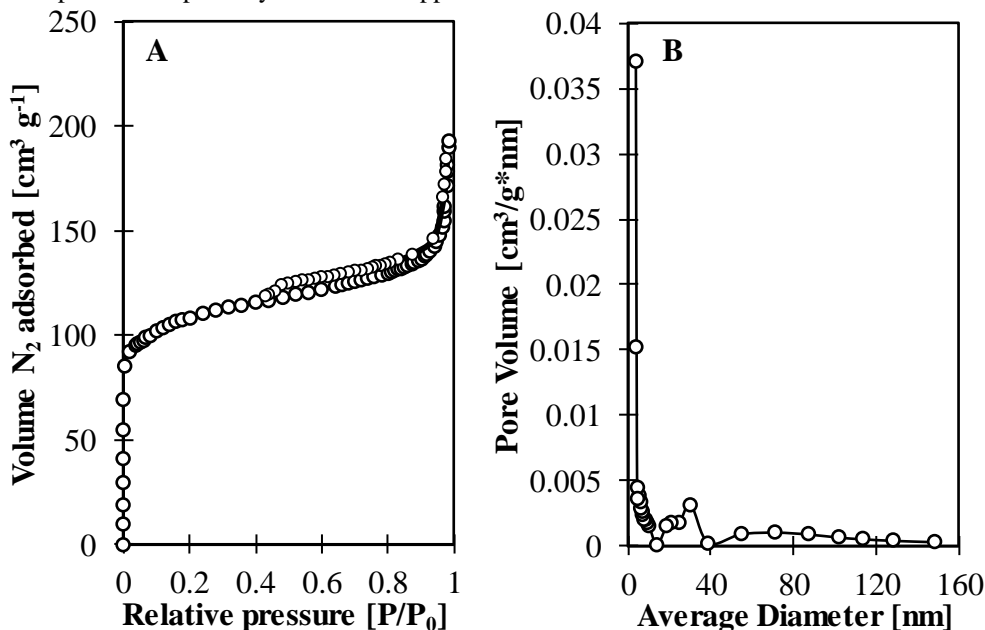


Fig. 3 (A) Nitrogen adsorption-desorption isotherm and (B) pore size distribution of 5Ni/HZSM-5.

increase at $P/P_0 = 0.9$. This isotherm showed the co-existence of both micro-mesoporosity in 5Ni/HZSM-5 catalyst. Pasupulety et al. [12] found that the molybdenum deposition was occurred in micro and mesopores of HZSM-5 with Si/Al ratio of 50 and 80 samples, which contributed to the happening of partially blockage and decreased the surface area of pristine different Si/Al ratio of HZSM-5 samples. Nonetheless, the structure of pristine HZSM-5 still preserved after molybdenum loading. In contrast, Chen et al. [13] reported on the loading of Ni onto highly siliceous HZSM-5 catalyst by using a deposition-precipitation method. After Ni deposition, they found that the alteration of isotherm from type H1 to H3 and an increased step at $P/P_0 > 0.4$, attributed to the presence of complex and irregular shape of mesopores that absent in the conventional HZSM-5 zeolite. Additionally, the Barrett, Joyner, and Halenda (BJH) method was employed to determine the pore size distribution of 5Ni/HZSM-5 catalyst. The main pore size distribution of 5Ni/HZSM-5 catalyst showed at 5-40 nm.

Surface basicity characterization was carried out with the use of FTIR adsorbed pyrrole analysis. Fig. 4(A) and (B) reveals the FTIR spectra of activated catalyst and pyrrole-adsorbed on activated catalyst at different outgassing temperatures, respectively. The activated catalyst presented several bands at 3710, 3610 and 3500 cm⁻¹, can be associated with the isolated external surface silanol (Si-OH) groups, bridging Si-OH-Al groups and hydroxyl nests comprising of a variety of silanol groups that interact well with extended hydrogen bonding or silanol defects [14]. The 5Ni/HZSM-5 showed a intense band at 3478 cm⁻¹, resulting from the interaction between pyrrole molecules and basic oxygen atoms of zeolite framework (C₄H₄NH-O_{zeolite}) [15].

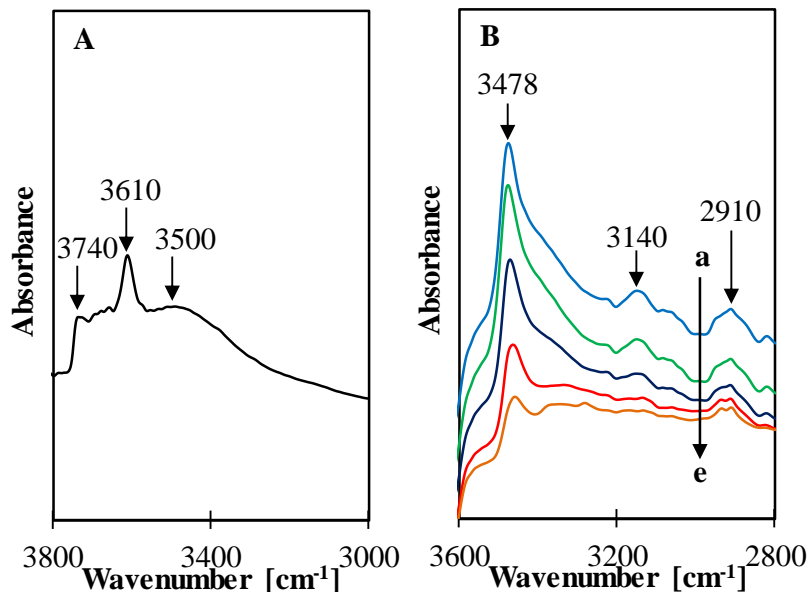


Fig. 4 FTIR spectra of (A) activated 5Ni/HZSM-5 catalyst at 400 °C and (B) activated adsorbed pyrrole catalysts at room temperature, subsequently outgassed at (a) room temperature, (b) 50 °C, (c) 100 °C, (d) 150 °C, and (e) 200 °C.

Moreover, the bands of medium strength liquid phase pyrrole and fundamental aliphatic $\nu(\text{CH})$ vibration were observed at 3140 and 2910 cm^{-1} , respectively [6]. Besides, the C-H stretching vibrations also shown in weak shoulder peaks at 2800-3100 cm^{-1} . The high intense of the peak signifies the presence of large number of basic sites. However, with increasing desorption temperature, the intensity of all peaks decreased sequentially, indicating there is reduction in the amount and strength of basic sites. Fig. 5 demonstrates the catalytic performance of 5Ni/HZSM-5 in the reaction temperature of 150-450 °C. Without Ni, HZSM-5 only has poor performance (not shown). It is noteworthy that the increase in the CO conversion and CH_4 yield were observed with the increasing in reaction temperature. The 5Ni/HZSM-5 catalyst achieved 100% conversion at low reaction temperature of 350 °C. It should be noted that the yield of CH_4 obtained is 96.4% at 350 °C and increased to 99.6% at 450 °C, with only negligible amount of CO_2 yield detected. Throughout the reaction temperature range, the yield of CO_2 is less than 4%. This indicated that only mild occurrence of water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$).

The good CO methanation performance of 5Ni/HZSM-5 can be related to the synergy influence between the presence of nickel metal with small crystallite size, micro-mesoporosity to facilitate the reactant's accessibility to active sites and material's high basicity. Guo et al. [16] presented the different type of Ni-based mesoporous supports on CO_2 methanation. The great performance was found on Ni/ZSM-5 catalyst because of the

basicity, Ni particle size and Ni metal-support synergistic effect.

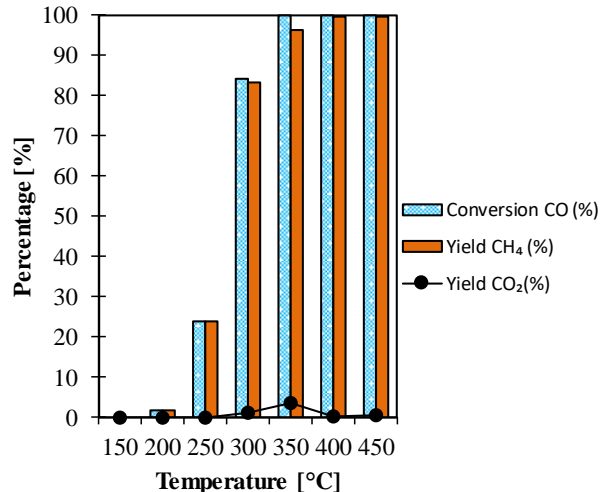


Fig. 5 Catalytic activity of 5Ni/HZSM-5 at 150-450 °C.

Contrastingly, Bacariza et al. [17] reported relationship of different Ni/zeolite framework type on the catalytic CO_2 methanation efficiency. They found that the smallest average Ni^0 size for favorable dispersion and presence of mesoporosity to accommodate Ni species was influenced by the zeolite framework type and both criteria played a vital role in determining of CO_2 methanation performance.

4. CONCLUSION

The present work investigated on the correlation between physicochemical properties and catalytic performance of 5Ni/HZSM-5 towards carbon monoxide methanation. The characterization of the samples by XRD, N₂ physisorption and FTIR adsorbed pyrrole techniques indicated that the existence of high crystallinity, micro-mesoporosity and high basicity of the 5Ni/HZSM-5 together with the beneficial implication of nickel addition had great potential in CO methanation to produce methane (CO conversion = 100% and CH₄ yield = 96.4%) at low temperature of 350 °C.

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