

CARBON DIOXIDE REFORMING OF METHANE OVER Ni/ γ -Al₂O₃, Ni/ZSM-5, Co/ γ -Al₂O₃ & Co/ZSM5

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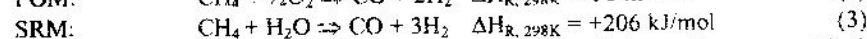
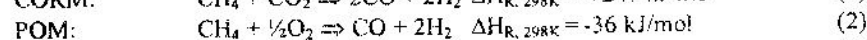
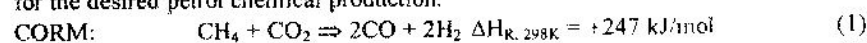
ABSTRACT

The catalytic performance of carbon dioxide reforming of methane to synthesis gas (H₂+CO) was studied over Ni/ γ -Al₂O₃, Ni/ZSM-5, Co/ γ -Al₂O₃ and Co/ZSM5. These catalysts were prepared using the incipient wetness impregnation method with 1 wt % of the metal. The catalysts were characterized using X-Ray Diffraction (XRD). The performance of the catalysts was tested in a lab-scale fixed-bed reactor with a reactant feed ratio of CH₄:CO₂ = 1:1, and F/W = 22,000 mL/g.hr. 1 g catalyst was loaded into the reactor for five hours of testing using 300 mL/min N₂ as the diluent. The experimental result displayed that the methane and carbon dioxide conversion decreased in the order: Co/ γ -Al₂O₃ > Ni/ γ -Al₂O₃ > Co/ZSM-5 > Ni/ZSM5, the CO production and selectivity decreased in the order: Ni/ γ -Al₂O₃ > Co/ZSM5 > Ni/ZSM5 > Co/ γ -Al₂O₃ and catalyst stability decreased in the order: Co/ZSM5 > Co/ γ -Al₂O₃ > Ni/ZSM5 > Ni/ γ -Al₂O₃. From the experimental result, Co/ZSM5 exhibited a good performance in catalyst activity and stability.

Keywords: ZSM5, Carbon Dioxide Reforming, Natural Gas, Catalytic Conversion.

INTRODUCTION

Carbon dioxide reforming of methane (CORM) is one of the interesting routes for the production of synthesis gas. Synthesis gas, a mixture of carbon monoxide and hydrogen can be produced from steam reforming of methane (SRM), partial oxidation of methane (POM) and carbon dioxide reforming of methane (CORM). These processes form the OH* and CH₃* as the preliminary intermediates in the synthesis gas mechanism [1]. Gas liquefaction will be carried on through the Fischer-Tropsch process for the desired petrol chemical production.



Reaction (1) produces the highest concentration of CO in synthesis gas with the ratio of CO:H₂ = 1:1. In reaction (2), the CO:H₂ produced through this reaction path is the most suitable composition for methanol production. The third reaction produces the lowest concentration of CO in synthesis gas due to the water gas shift reaction. Both reforming processes are highly endothermic while oxidation process is the exothermic.

Numerous papers have been published on CORM about the deactivation of catalyst due to carbon deposition, coking and catalyst sintering at higher operating temperature [2]. This is because the operating temperature of the CORM (550° C - 800° C) overlaps with the temperature of carbonaceous residues through the Boudouard Reaction (500° C - 700° C). The reaction schemes are presented in eqs (4) and (5).



Carbonaceous residues will cover the active sites and block the pore of the catalyst, and deactivates the catalyst [2]. As a result, CORM is not the preferred method for synthesis gas production. One of the solutions for this problem is to add oxygen as a coke removal agent to gasify the carbonaceous residues before it invades the surface of the catalyst [3,6-9]. Park [10] and Chin & Amin [11] concluded that the pentasil-type zeolite could be used as a support for metal catalysts in the CORM. The purpose of this research is to determine the possibility of modified ZSM5 in CO₂-CH₄ reaction. In this study, we tried to compare the Ni and Co supported with γ -Al₂O₃ and ZSM5.

CATALYST PREPARATION AND CHARACTERIZATION

1 wt % M/S (M = Ni [Merck] & Co [R & M Chemicals], S = γ - Al_2O_3 [Merck] & ZSM5 [Zeolyst International]) was prepared by impregnating S with $\text{M}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solution. The weight ratio M/S is 1/100. The mixture is dried overnight in an oven at 100° C and then calcined for five hours at 550° C. The specifications of ZSM-5 (Zeolyst International-CBV 3024E) are $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$, Na_2O weight % = 0.05 and surface area = 400 m^2/g .

The modified catalyst is then characterized using X-ray Diffraction (XRD) Siemen D5000 with 0.050°, 1.0s step time, $5^\circ < 2\theta < 60^\circ$ and Cu anode. The modified catalyst will be directly compared with the original support.

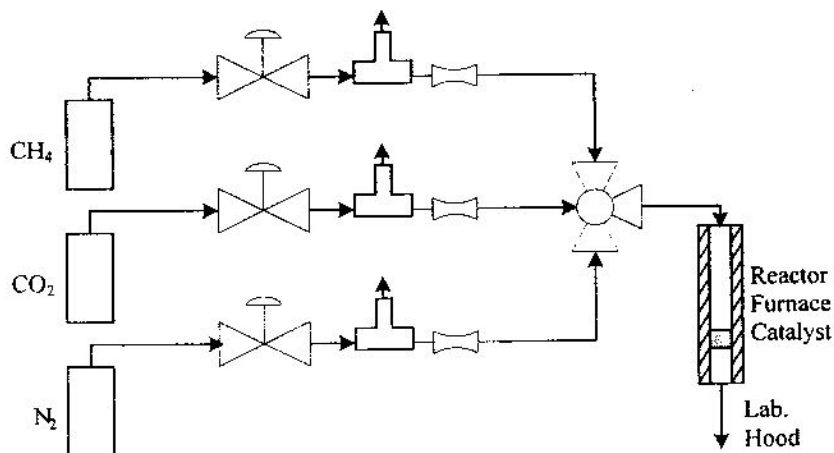


Figure 1. Schematic diagram of the experiment setup

PERFORMANCE OF CATALYST

The experiment was conducted with $\text{CH}_4:\text{CO}_2:\text{N}_2 = 1:1:6$, at F/W = 22,000 ml/g.hr , 1.00 g catalyst, temperature 800° C and pressure 1atm. The reactor is preheated with N_2 gas for two hours to activate the catalyst. Figure 1 shows the schematic diagram of the experimental equipment. The gaseous products were analyzed by CO-O_2 Gas Analyzer (Kane May).

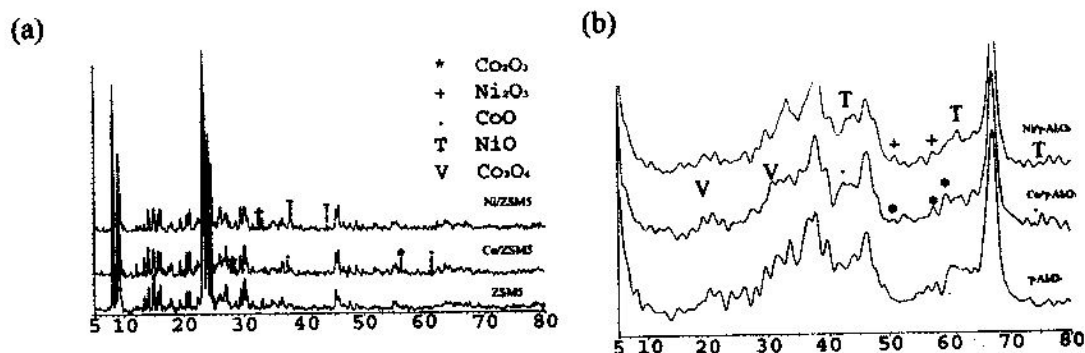


Figure 2. The XRD result from the (a) Original ZSM-5 and modified ZSM5 (b) Original γ - Al_2O_3 and modified γ - Al_2O_3

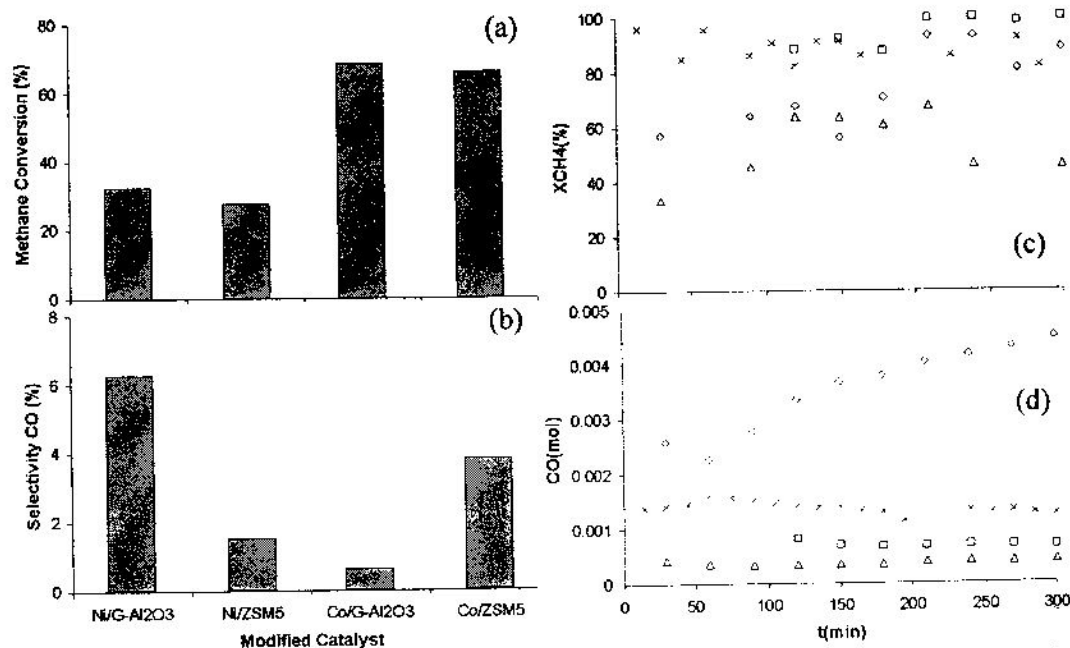


Figure 3. Profile of various catalyst performance. Condition: 1 atm, 800° C, CH₄: CO₂:N₂ = 1:1:6 and F/W = 22,000 mL/g.hr. a) Accumulative X_{CH₄} for the different catalyst. b) Accumulative S_{CO/CH₄} for the different catalyst. c) X_{CH₄} versus TOS. d) CO production versus TOS. ○: Ni/γ-Al₂O₃, □: Ni/ZSM5, △: Co/γ-Al₂O₃, X: Co/ZSM5

RESULT AND DISCUSSION

Catalyst Characterization - XRD

In Figure 2, 2θ location of the peaks indicated the modified catalyst has the same characteristics with the original catalysts but the intensities are different. In Figure 2a, the modified ZSM5 are compared with its parent ZSM5 XRD pattern. * peaks on 2θ = 27.9, 56.4 and • peaks on 2θ = 36.5, 61.4 in Co/ZSM5 are identified as the crystalline phase of Co₂O₃ and CoO, respectively. + peaks on 2θ = 32.0 and T peaks on 2θ = 37.2, 43.2 in Ni/ZSM5 are crystalline phase of Ni₂O₃ and NiO, respectively. In Figure 2b, the modified γ-Al₂O₃ are compared with the original γ-Al₂O₃ XRD diffractograph. V peaks on 2θ = 19.0, 31.2, • peaks on 2θ = 42.4, 73.6 and * peaks on 2θ = 51.3, 56.4, 58.88 on the Co/γ-Al₂O₃ are identified as the crystalline phase of Co₃O₄, CoO and Co₂O₃, respectively. The presence of Co₃O₄ in the Co/γ-Al₂O₃ gives different characteristic to its reactivity. T peaks on 2θ = 43.2, 62.9, 75.3 and 2θ = 51.5, 56.8 on the Ni/γ-Al₂O₃ are identified as the crystalline phase of NiO and Ni₂O₃, respectively. This indicates that the modified catalyst has been successfully impregnated with the desired metal. The XRD pattern results demonstrate that the framework of original catalyst did not collapse as a result of impregnating it with Mⁿ⁺ ions.

Catalyst Activity - Overall Performance in Conversion and Selectivity

Variation with four catalysts of average X_{CH₄} and S_{CO/CH₄} are shown in Figure 3a and 3b. The accumulative properties are defined as below:

$$\bar{X}_{CH_4} = \frac{\int_a^b X_{CH_4}(t) dt}{b-a}, \bar{S}_{\frac{CO}{CH_4}} = \frac{\int_a^b S_{\frac{CO}{CH_4}}(t) dt}{b-a}. \text{ Where } X_{CH_4}(t) \text{ and } S_{\frac{CO}{CH_4}}(t) \text{ are}$$

$$X_{CH_4} = \frac{n_{i,CH_4} - n_{o,CH_4}}{n_{i,CH_4}} \times 100\%, S_{\frac{CO}{CH_4}} = \frac{n_{o,CO}}{n_{i,CH_4} - n_{o,CH_4}} \times 100\%$$

In Figure 3a, average X_{CH₄} over Co/γ-Al₂O₃ has been found to be the highest among the other samples. However, the average S_{CO/CH₄} for Co/γ-Al₂O₃ is the lowest. This is related to its particular properties as indicated in the XRD results of this sample (Co₃O₄ crystalline phase present in the sample, but absent in Co/ZSM5, see Figure 2b). From Figure 3a and 3b, it could be observed that Ni/γ-

Al₂O₃ catalyst is suitable for the synthesis gas production because most of the reacted atom carbon has been distributed to the CO formation. It is expected that the whole process produce the other products beside synthesis gas from the high methane conversion and low CO selectivity catalyst such as Ni/ZSM5 and Co/ γ -Al₂O₃. The side products may be consist of the higher hydrocarbons (HHCs) or other oxygenates. This co-generation of synthesis gas and other side-products is studies.

Catalyst Activity – Potential of ZSM5 in Higher Hydrocarbons (HHCs)

From the reaction (1), it is clear that the stoichiometry ratio of CO/H₂ should be 1.000. The experimental CO/H₂' ratio in Table 1 is lower than 1.000. This result indicates that the Ni/ZSM5, Co/ZSM5 and Co/ γ -Al₂O₃ have other side-products. This is because the reacted atom carbon has distributed to other side-products (such as HHCs, MeOH, and others). This is because the porous ZSM-5 has a high BET and shape selective zigzag pore, which encourages the oligomerization of methyl radical into HHCs. Besides that, CO₂ is a good oxidant agent which encourages the CH_x' formation. Further more, CO₂ does not react with CH_x.

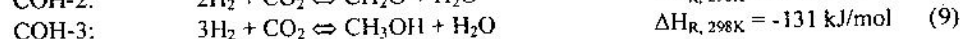
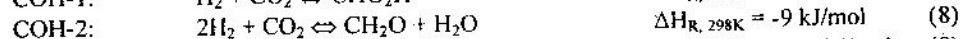
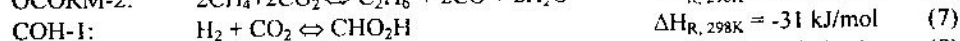
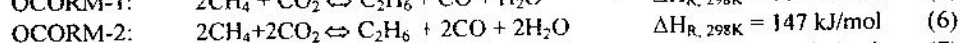
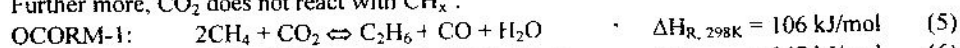


Table 1. Ratio of CO/H₂' and the ratio of n_{o,CO}(t=300min)/n_{o,CO}(t=30min) of several catalyst

Catalyst	CO/H ₂ '	n _{o,CO} (t=30min)	n _{o,CO} (t=300min)	n _{o,CO} (t=300min)/ n _{o,CO} (t=30min), a	Stability = [1-a] _{abs}	Coke Rate ($\mu\text{mol/g}_{\text{cat}}\cdot\text{min}$)
Ni/ γ -Al ₂ O ₃	1.000	0.00258	0.00448	1.739	0.739	322
Ni/ZSM5	0.258	0.00081*	0.000666	0.826	0.174	273
Co/ γ -Al ₂ O ₃	0.013	0.00042	0.000357	0.850	0.150	393
Co/ZSM5	0.051	0.00141	0.001247	0.887	0.113	83

* n_{o,CO}(t=120min).

Catalyst Activity – Effect of Time of Stream (TOS)

Figure 3c shows the catalyst activity profile versus time on stream (TOS). Methane conversion of Ni/ZSM5 and Co/ZSM5 are very high and stable. This is because the ZSM5's BET ($\pm 400 \text{ m}^2/\text{g}$) is much more higher than γ -Al₂O₃ ($\pm 165 \text{ m}^2/\text{g}$), see figure 4. Along the TOS, X_{CH₄} of Ni/ γ -Al₂O₃ is increasing while Co/ γ -Al₂O₃ decreases after t = 210 min. This is because the Co₃O₄ crystalline phase in Co/ γ -Al₂O₃ deactivates the catalyst performance.

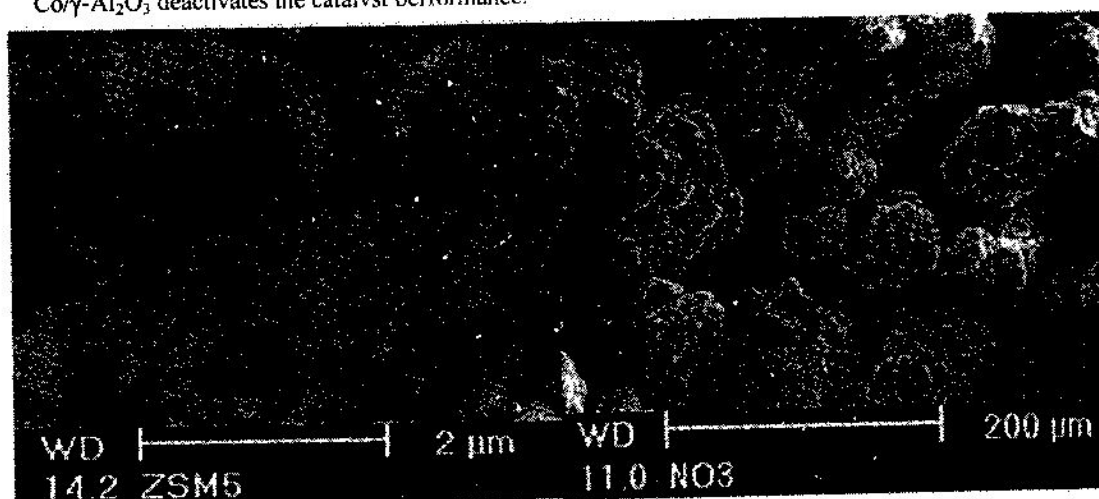


Figure 4. SEM for a) ZSM5, magnification: 10,000 X. b) γ -Al₂O₃, magnification: 125 X.

Catalyst Activity – Stability Factor & Stability

Figure 3d demonstrates the CO production profile versus TOS. To determine the reaction stability, factor $n_{o,CO}(t=300\text{min})/n_{o,CO}(t=30\text{min})$ is introduced (see Table 1).

$$\text{Stability Factor, } a = \frac{n_{o,CO}|_{t=300\text{ min}}}{n_{o,CO}|_{t=30\text{ min}}}$$

Stability Factor close to 1.00 means CO production rates from Ni/ZSM5, Co/ γ -Al₂O₃ and Co/ZSM5 are very stable. Stability Factor over 1.00 means CO production is continuously increasing while below 1.00 is continuously decreasing. Another parameter is also introduced to study the stability comparison among the catalysts.

The stability is defined as:

$$\text{Stability} = |1 - a|_{\text{abs}}$$

Small number of stability gives a stable catalyst performance. The stabilities of the catalysts order are: Co/ZSM5 > Co/ γ -Al₂O₃ > Ni/ZSM5 > Ni/ γ -Al₂O₃. Low coke rate of Co/ZSM5, 83 $\mu\text{mol coke/g}_{\text{cat}}\cdot\text{min}$ in the Table 1 proves that the stability calculation is correct.

Catalyst Activity – Ni/ γ -Al₂O₃

Low stability of Ni/ γ -Al₂O₃ does not mean that the catalyst is not good for the CORM. Figure 3d shows us that the CO is still increasing after $t = 300$ min TOS. Its CO production and coke rate exhibits that Ni/ γ -Al₂O₃ has its ability to react continuously although coke deposited on it. The reactivity is still keeping on. This means that Ni/ γ -Al₂O₃ has a largest carbonaceous capacity to be well-operated after 300 minutes. On the other words, high carbon deposition rate does not block or cover the active site on Ni/ γ -Al₂O₃.

CONCLUSION

1. Co₃O₄ crystalline phase identified in the Co/ γ -Al₂O₃ gives activity effects to X_{CH₄} and S_{CO}. It can be concluded that the different crystalline phase is produced on the different catalyst support although the catalysts are prepared with the same metal in the same condition.
2. Reactivity comparison:
X_{CH₄} & X_{CO₂} decreases in order: Co/ γ -Al₂O₃ > Ni/ γ -Al₂O₃ > Co/ZSM-5 > Ni/ZSM5,
N_{CO}, S_{CO/CH₄} & Y_{CO/CH₄} decreases in order: Ni/ γ -Al₂O₃ > Co/ZSM5 > Ni/ZSM5 > Co/ γ -Al₂O₃,
Catalyst stability decreases in the order: Co/ZSM5 > Co/ γ -Al₂O₃ > Ni/ZSM5 > Ni/ γ -Al₂O₃.
From the experimental result, Co/ZSM5 exhibited a good performance in catalyst activity and stability. The advantages of Co/ZSM5 are Co₂O₃ suppresses coke formation and has a high surface area.
3. The experimental H₂/CO ratio indicates that the ZSM5 has its potential to produce other valuable products such as HHCs, alcohols, Aldehyde and acid. This can be concluded that ZSM5 based catalyst is suitable for Oxo-carbon dioxide reforming of methane (OCORM) and carbon dioxide hydrogenation (COH).
4. Ni/ γ -Al₂O₃ is suitable for the CORM although the catalyst has a low stability. However, the positive Stability Factor indicates that the catalyst needs a longer time to reach the equilibrium. Beside that, it has the highest CO production and a large capacity of carbonaceous deposition.

NOTATION AND ABBREVIATION

BR	Boudouard Reaction
CORM	Carbon dioxide reforming of methane
COH	Carbon dioxide hydrogenation
F	Feed flow rate, mL/min
HHCs	Hydrocarbons
M ⁿ⁺	Metal with n kation
OCM	Oxidative coupling of methane
OCORM	Oxo-carbon dioxide reforming of methane
POM	Partial oxidation of methane
S	Selectivity, dimensionless
SEM	Scanning Electronic Microscopic

SRM	Steam reforming of methane
TOS	Time on Stream, minute
W	Catalyst weight, g
X	Conversion, dimensionless
XRD	X-ray Diffraction
Y	Yield

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