

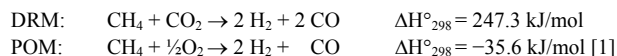
Syngas Production by Oxy-CO₂ Reforming of Methane over PdNi Catalyst

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Introduction

Enormous efforts have been taken to utilize CO₂ as an important element for suitable future development since it is the important source of carbon and chemical feedstock in the future [1]. It can be used to produce syngas with methane as the co-feed via CO₂ reforming of methane. This reaction is one of the potential solutions to reduce CO₂ and CH₄ (the two largest greenhouse effect gases [2]) in large quantities. However, rapid carbon deposition is the most serious problem preventing commercialization of this reaction in industries. The carbon deposition easily deactivates the catalyst in relatively short time. Another drawback is high energy requirement in this reaction leading to high cost. To overcome these drawbacks, partial oxidation of methane (POM) is combined with CO₂ (dry) reforming of methane (DRM), these reactions are:



Combination of these reactions can reduce the amount of carbon deposition since the oxygen easily oxidizes the deposited carbon on the catalyst. It can also reduce total energy requirement since it combines exothermic (POM) and endothermic (DRM) reactions.

Materials and Methods

PdNi-catalysts over several commercial metal oxides as the catalyst supports are synthesized using incipient wet impregnation method. For comparison, Ni and Pd catalysts are also synthesized over the best support in this study. The catalytic activities are investigated at different reaction temperatures between 500-800°C and at different feed ratios in a fixed-bed continuous-flow reactor. Some characterization methods such as BET, XRD, TPR, TPO, XPS, TGA, and FESEM are employed to study them in details.

Results and Discussion

It can be seen from the results shown in Table 1 that the catalytic performance decreases in the order of PdNi/Y₂O₃ > PdNi/Al₂O₃ > PdNi/La₂O₃ > PdNi/CeO₂ > PdNi/SiO₂ > PdNi/TiO₂. PdNi/Y₂O₃ shows the highest conversion of CH₄ and CO₂ and it also shows very stable performance without noticeable deactivation over 8 hour reaction time. Meanwhile, PdNi/TiO₂ shows negative conversions of CO₂. This indicates that the methane combustion is favored for this support. It should be noted that the oxygen conversion is always 100% in all experimental runs.

Since CO₂ reforming of methane can easily produce carbon, hence, the amount of deposited carbon can be measured using TGA apparatus. The TGA results show that the

amount of deposited carbon increases in the order of PdNi/Y₂O₃ < PdNi/Al₂O₃ < PdNi/La₂O₃ < PdNi/TiO₂ < PdNi/CeO₂ < PdNi/SiO₂. This order is reversed compared with the catalytic performance. Therefore, it can be concluded that deposited carbon is the main cause of rapid deactivation of PdNi/La₂O₃, PdNi/TiO₂, PdNi/CeO₂ and PdNi/SiO₂.

Table 1. PdNi catalyst performance over several supports

Supports	Product composition (after 8 hours)				Conversion (%)		H ₂ /CO
	H ₂	CO	CH ₄	CO ₂	CH ₄	CO ₂	
γ-Al ₂ O ₃	51.62	25.02	9.36	14.00	81.29	44.01	2.06
SiO ₂ ¹	54.05	14.66	9.33	21.95	81.33	12.19	3.69
TiO ₂ ¹	35.93	16.47	13.51	34.09	72.97	-36.36	2.18
La ₂ O ₃ ²	62.28	20.48	11.72	5.42	76.56	77.94	3.04
Y ₂ O ₃	55.05	28.79	6.24	9.92	87.52	60.33	1.91
CeO ₂ ¹	58.01	25.00	6.90	10.09	86.19	59.65	2.32

Note: Reaction conditions: P_{total} 1 atm, T = 700°C, CH₄/CO₂/O₂ = 2/1/1, GHSV = 12000 cm³/g/h, reactor plugged after 1.5 hours¹ and 7.5 hours²

As PdNi/Y₂O₃ shows lower H₂/CO ratio than PdNi/La₂O₃, it is therefore chosen for further study on the effects of reaction temperature (500°C, 600°C, 700°C and 800°C) and feed ratio (CH₄/CO₂/O₂/He: 10/5/5/-, 5/10/5/-, 5/5/5/5, 5/5/3/7, 5/10/1/4). The results show that H₂ and CO yields increase with increasing temperature. While CH₄ and CO₂ conversions also increase with increasing temperature, but the increase is more dramatic for CO₂. These trends are expected as the higher the operating temperature the higher the activity of the catalyst is. However, it is observed that at temperature 600°C and below, the CO₂ conversion becomes negative. This indicates that methane combustion is more dominant than other possible reactions at lower temperature. It can be explained from thermodynamics since the combustion reaction is exothermic which favors at lower temperature. The very high H₂/CO ratios also confirm this explanation.

The results from feed ratio study show that the CH₄ conversion decreases with increasing CH₄ due to excess of CH₄. While H₂/CO ratio increases with increasing CH₄ as the partial oxidation of methane becomes more dominant. The same trend is observed when CO₂ increases. The CO₂ conversion and H₂/CO ratio decrease due to excess of CO₂ which favors dry reforming of methane. Meanwhile, CH₄ conversion decreases and at the same time CO₂ conversion increases with decreasing O₂, causing a decrease in H₂/CO ratio.

Significance

This study shows an alternative route to produce different ratios of syngas (1.05 to 1.99) using oxy-CO₂ reforming of methane by varying feed ratio. This reaction overcomes the deactivation of catalyst due to deposited carbon problem in DRM and due to hotspot problem in POM.

References

1. Chunsan, S. and Wei Pan, *Catalysis Today* 98, 463-484 (2004).
2. Annual Review Energy 2006, www.eia.doe.gov