Syngas Production by Oxy-CO_2 Reforming of Methane over PdNi Catalyst

Usman O., S. Kawi and K. Hidajat*
Department of Chemical and Biomolecular Engineering
National University of Singapore, 4 Engineering Drive 4, Singapore 117576
*chehidak@nus.edu.sg

Introduction

Enormous efforts have been taken to utilize CO_2 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 CO_2 reforming of methane. This reaction is one of the potential solutions to reduce CO_2 and CH_4 (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 CO_2 (dry) reforming of methane (DRM), these reactions are:

DRM: $CH_4 + CO_2 \rightarrow 2\ H_2 + 2\ CO$ $\quad \Delta H°_{298} = 247.3$ kJ/mol
POM: $CH_4 + \frac{1}{2}O_2 \rightarrow 2\ H_2 + \ CO$ $\quad \Delta H°_{298} = -35.6$ kJ/mol [1]

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/Y_2O_3> PdNi/Al_2O_3> PdNi/La_2O_3> PdNi/CeO_2> PdNi/SiO_2> PdNi/TiO_2. PdNi/Y_2O_3 shows the highest conversion of CH_4 and CO_2 and it also shows very stable performance without noticeable deactivation over 8 hour reaction time. Meanwhile, PdNi/TiO_2 shows negative conversions of CO_2. 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 CO_2 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/Y_2O_3< PdNi/Al_2O_3< PdNi/La_2O_3< PdNi/TiO_2< PdNi/CeO_2< PdNi/SiO_2. 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/La_2O_3, PdNi/TiO_2, PdNi/CeO_2 and PdNi/SiO_2.

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_2O_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_2O_3[2]	62.28	20.48	11.72	5.42	76.56	77.94	3.04
Y_2O_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, $CH_4/CO_2/O_2$ = 2/1/1, GHSV = 12000 $cm^3/g/h$, reactor plugged after 1.5 hours[1] and 7.5 hours[2]

As PdNi/Y_2O_3 shows lower H_2/CO ratio than PdNi/La_2O_3, 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 ($CH_4/CO_2/O_2$/He:10/5/5/-,5/10/5/-, 5/5/5/5, 5/5/3/7, 5/10/1/4). The results show that H_2 and CO yields increase with increasing temperature. While CH_4 and CO_2 conversions also increase with increasing temperature, but the increase is more dramatic for CO_2. 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 CO_2 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 H_2/CO ratios also confirm this explanation.

The results from feed ratio study show that the CH_4 conversion decreases with increasing CH_4 due to excess of CH_4. While H_2/CO ratio increases with increasing CH_4 as the partial oxidation of methane becomes more dominant. The same trend is observed when CO_2 increases. The CO_2 conversion and H_2/CO ratio decrease due to excess of CO_2 which favors dry reforming of methane. Meanwhile, CH_4 conversion decreases and at the same time CO_2 conversion increases with decreasing O_2, causing a decrease in H_2/CO ratio.

Significance

This study shows an alternative route to produce different ratios of syngas (1.05 to 1.99) using oxy-CO_2 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

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