Combined Reforming of Methane over Supported Ni Catalysts

Hyun-Seog Roh[1], Kee Young Koo[2], Jin Hyeok Jeong[3], Yu Taek Seo[1], Dong Joo Seo[1], Yong-Seog Seo[1], Wang Lai Yoon[1]* and Seung Bin Park[2]
[1]*Korea Institute of Energy Research, Yuseong, Daejeon 305-343, Korea*
[2]*Korea Advanced Institute of Science and Technology, Yuseong, Daejeon 305-701, Korea*
[3]*Kyungpook National University, Buk-gu, Daegu 702-701, Korea*
*wlyoon@kier.re.kr

Introduction

Combined steam and carbon dioxide reforming of methane (CSCRM) offers great advantage to adjust H_2/CO ratio in the product synthesis gas by changing the feed $H_2O/CO_2/CH_4$ ratio to meet the requirements of Fischer-Tropsch and methanol syntheses [1]. Commercially, supported Ni catalysts have been used in SRM because Ni is economical compared with noble metal based catalysts [2]. However, supported Ni catalysts easily deactivate due to carbon formation in carbon dioxide reforming of methane (CRM) as well as in CSCRM. Recently, Xu and co-workers reported that the Ni catalyst supported by small nanoparticles of ZrO_2 or MgO could be highly active and stable for CRM [1,3]. In addition, Roh et al. reported that nano-sized Ni-Ce-ZrO_2 catalyst could be active and stable in CRM [4]. Thus, it is inferred that the size of NiO and support plays a significant role in CSCRM.

In this study, various supported Ni catalysts have been prepared and applied for CSCRM to achieve a H_2/CO ratio of 2, which is suitable for the Fischer-Tropsch and methanol syntheses. We report here that nano-sized Ni/MgO-Al_2O_3 catalyst exhibits the highest activity and stability among supported Ni catalysts in CSCRM.

Materials and Methods

Supports employed in this study were MgO-Al_2O_3 (MgO=30wt%), MgO, ZrO_2, CeO_2. MgO-Al_2O_3 support was prepared by pre-calcination of hydrotalcite material at 800 °C for 6 h. The others were also pre-calcined at 800 °C for 6 h. Supported Ni catalysts (Ni = 12 wt%) were prepared by the incipient wetness method with $Ni(NO_3)_2 \cdot 6H_2O$. The prepared catalysts were calcined at 800 °C for 6 h in air. Commercial Ni/α-alumina catalyst was employed as a reference in CSCRM. The crystallite size of NiO in prepared catalysts was estimated in XRD pattern using the Scherrer equation. Activity tests were carried out at 800 °C and 1 atm and space velocity of 265,000 cm^3 gas fed/g_{cat}-h in a fixed-bed micro-reactor. Prior to each catalytic measurement, the catalyst was reduced in 10% H_2/N_2 at 700 °C for 1 h. The reactant gas stream consisted of H_2O, CO_2, and CH_4. Water was fed using a syringe pump and was vaporized at 150 °C upstream of the reactor. The reformate was chilled, passed through a trap to condensate residual water, and then flowed to the on-line GC.

Results and Discussion

Supported Ni catalysts have been tested with $H_2O/CO_2/CH_4$ ratio of 0.8/0.4/1.0 because H_2/CO ratio of 2 has been obtained in the product gas. The reaction results for CH_4 conversion with time on stream are presented in Figure 1. It is clear that Ni/MgO-Al_2O_3 catalyst exhibited the highest CH_4 conversion and the activity was maintained for around 20 h of time of stream. In the case of commercial Ni/α-alumina catalyst, the catalyst rapidly deactivated with time on stream due to carbon formation. This is due to the fact that the commercial catalyst has been optimized for SRM, which uses excess steam to prevent coke formation [2]. Ni/MgO and Ni/ZrO_2 showed about 60% and 70% CH_4 conversion, respectively. Ni/CeO_2 showed initially 57% CH_4 conversion, and it gradually decreased to 50% and it was maintained. It is interesting to note that Ni/CeO_2, which has the largest NiO size (55 nm), showed the lowest CH_4 conversion, while Ni/MgO-Al_2O_3 with the smallest NiO size (less than 3 nm) exhibited the highest CH_4 conversion. The other catalysts, which have NiO size between 20 and 30 nm, initially showed 60 – 70% CH_4 conversion. Thus, it can be speculated that there is a relationship between activity and NiO crystallite size of the catalyst. Further work is underway to confirm it.

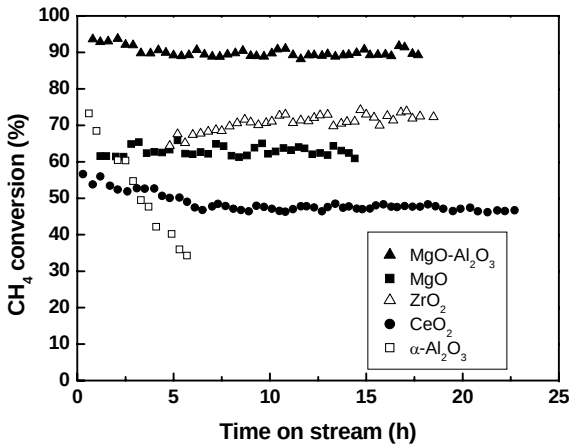

Figure 1. CH_4 conversion with time on stream over supported Ni catalysts (T=800°C, $H_2O/CO_2/CH_4$ ratio of 0.8/0.4/1.0).

Significance

Ni/MgO-Al_2O_3 can be a good candidate catalyst for CSCRM due to the highest activity as well as stability among the tested Ni catalysts.

References

1. Zhang, Q.-H., Li, Y., and Xu, B.-Q., *Catal. Today* 98, 601 (2004).
2. Rostrup-Nielsen, J.R. in "Catalysis, Science and Technology" (J.R. Anderson, and M. Boudart, Ed.) Vol. 5, Chap. 1. Springer-Verlag, Berlin, 1984.
3. Xu, B.-Q., Wei, J.-M., Wang, H.-Y., Sun, K.-Q., and Zhu, Q.-M., *Catal. Today* 68, 217 (2001).
4. Roh, H.-S., Potdar, H.S., and Jun, K.-W., *Catal. Today* 93-95, 39 (2004).