

Accumulation of the Carbonaceous Species on the Ni/Al₂O₃ Catalyst during CO₂ Reforming of Methane

Jae-Hee Lee, Oh-Shim Joo, Young-Soon Baek,[†] Yong Ho Yu,[‡] and Kwang-Deog Jung*

Nano-Eco Research Center, Korea Institute of Science and Technology, P.O. Box 131, Seoul 136-791, Korea

[†]LNG Technology Research Center, Korea Gas Corporation, Dongchun-Dong, Yeonsu-Ku, Incheon 406-130, Korea

[‡]Samsung Engineering Co., R&D Center, Doosan Bldg, 39-3, Sungbok-Ri, Suji-Eup, Yongin-si, Gyunggi-Do 449-844, Korea

Received March 28, 2003

The dependency of the rate of CO₂ reforming of methane on the catalyst loading and the reactor size was examined at a fixed temperature of 750 °C and a fixed GHSV of 18000 mL(STP)/g_{cat}·h. The conversion of methane in CO₂ reforming decreased with increase in the reactor size. The catalyst was severely deactivated with increase in the catalyst amount. The amount of carbonaceous species combustible below 550 °C, determined by TPO experiments with the used catalyst samples increased with increase in the catalyst amount, which was again confirmed by XRD and TEM experiments. The increase of the carbonaceous species combustible below 550 °C may be due to the suppression of the reverse Boudouard reaction, since the CO₂ reforming of methane, a highly endothermic reaction, resulted in lowering the reaction temperature.

Key Words : CO₂ reforming, NiAl₂O₄ catalyst, Coke formation, TPO

Introduction

CO₂ reforming of methane has attracted a great interest for several decades since it produces the CO/H₂ ratio suitable for the synthesis of liquid fuel such as higher hydrocarbons and oxygenated derivatives.¹⁻⁸ Additionally, CO₂ reforming can be used in chemical energy transmission systems.⁹⁻¹⁰ A number of supported catalysts have been studied for CO₂ reforming of methane. It was reported that supported noble metal catalysts were highly active and stable in the reaction, but supported Ni catalysts were extensively studied from a practical point of view.^{11,12} However, the supported Ni catalysts were severely deactivated and coke formation was regarded as the main cause of deactivation during CO₂ reforming of methane. Coke formation could be suppressed by using the supports such as i) MgO,^{13,14} ii) ZrO₂,¹⁵ iii) lanthania,¹⁶ and iv) the solid solution (MgAl₂O₄)^{17,18} and by modifying Ni-supported catalysts such as by i) sulfidation,¹⁹ ii) ceria addition,²⁰⁻²² and iii) Mn addition.²³ Nonetheless, the importance of the state of the nickel phase was more emphasized than that of the support effects and the additive effects.^{24,25} Coke formation was dependent on the reactor type in practical use. The effect of the reactor type was discussed in terms of carbon deposition by the endothermic heat of CO₂ reforming.^{26,27} In other words, it was observed that coke formation was dependent on the catalyst amount and the reactor size for the Ni/Al₂O₃ catalysts in CO₂ reforming of methane in this work. The main reason for the experimental results was put forward.

Experimental Section

A CO₂ reforming catalyst (10 wt% Ni/Al₂O₃) was prepared

by impregnating γ -Al₂O₃ support with Ni nitrate solution as previously reported.²⁵ The dried samples were calcined at 800 °C for 16 h. The prepared catalyst (200-300 mesh) was charged in an inconel tubular reactor and then reduced in-situ at 800 °C for 3 h in 5% H₂/Ar (60 mL/min). Two reactors with the diameter of 1/4" and 3/8" were used for CO₂ reforming of methane. A thermocouple was positioned on top of the catalyst bed to control the reaction temperature.

CO₂ reforming of methane was conducted at 750 °C and 18000 mL(STD)/g_{cat}·h in a stream of CO₂/CH₄=1/1. The products composed of H₂, CO, CH₄ and CO₂ were analyzed by an on-line GC (Young-Lin, M600D) with a carbosphere column (1/4" × 3 m), where Ar was the carrier gas of GC. Coke deposition after 16 h reaction was quantitatively analyzed by an elemental analyzer (FISON S Ind.). Temperature programmed oxidation (TPO) was performed for the used samples in a stream of 30% O₂/He with a ramping rate of 20 °C/min. The product gases were monitored with a mass detector (Balzers, MS-Cube 200). TEM images of the used catalysts were obtained by a Phillips CM-30 scanning transmission electron microscopy. The specimens were prepared by a suspension on the holes of a carbon grid.

Results and Discussion

The structure of the prepared Ni/Al₂O₃ catalyst was confirmed to be a NiAl₂O₄ phase by TPR (temperature-programmed reduction) as previously reported.²² CO₂ reforming of methane was conducted with a GHSV of 18000 mL (STD)/g_{cat}·h at 750 °C for 16 h after reducing the NiAl₂O₄ sample to Ni/Al₂O₃. Figure 1 shows the conversion of methane against the reaction time with 50 mg, 100 mg and 200 mg of the catalyst. The initial conversion of methane decreased with increase in the amount of the catalyst charged in the reactor. The steady conversion of

*Corresponding author. e-mail: jkdcatt@kist.re.kr

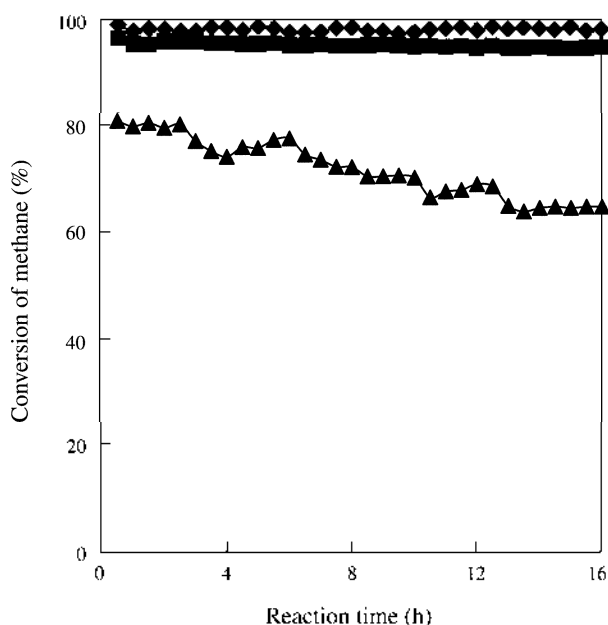


Figure 1. Catalytic activity and stability of 10 wt% Ni/Al₂O₃ catalyst in a 1/4" reactor with different catalyst amount (T=750 °C, CH₄/CO₂ 1.0, GHSV 18000 mL/g_{cat}.h): (◆) 50 mg, (■) 100 mg, (▲) 200 mg.

methane was maintained for 16 h with 50 mg of the catalyst, but it steadily decreased with 200 mg.

The different activity with different catalyst amount under the apparently same reaction temperature and GHSV indicates that the reaction rate of CO₂ reforming would not be described by intrinsic kinetics. For further investigation, the reactor size was changed from a 1/4" inconel tube to a 3/8" inconel tube. Figure 2 shows the methane conversion

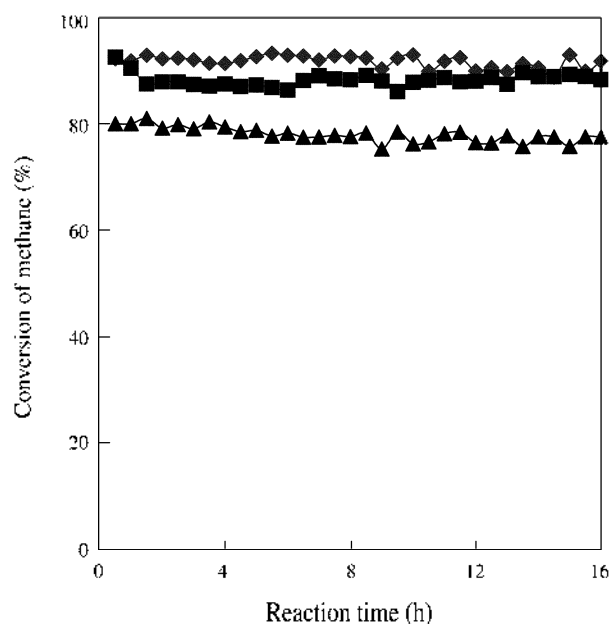


Figure 2. Catalytic activity and stability of 10 wt% Ni/Al₂O₃ catalyst in a 3/8" reactor (T=750 °C, CH₄/CO₂=1.0, GHSV=18000 mL/g_{cat}.h): (◆) 50 mg, (■) 100 mg, (▲) 200 mg.

Table 1. The quantitative carbon analysis of the used catalyst samples at 750 °C for 16 h

Amount of catalyst charged (mg)	Carbon deposition after 16 h reaction (wt%)
50	0.6
100	1.5
200	2.6

against the reaction time with the catalyst amounts of 50 mg, 100 mg and 200 mg in the 3/8" reactor.

The initial conversion of methane was maintained for 16 h even with 200 mg of catalysts in the reactor of 3/8" tube, which was different from the experimental result with the 1/4" reactor. The conversion of methane in the reactor of a 3/8" tube was slightly lower than that in the 1/4" reactor with the same amount of the catalyst. The effects of the reactor size and the catalyst amount may be due to the factors such as lateral diffusion, lateral heat transfer and axial temperature gradient resulting from the endothermic heat of reaction. The total carbon deposited on the Ni/Al₂O₃ catalyst after 16 h reaction in the reactor of 1/4" was analyzed. Table 1 shows that the specific carbon deposited on the catalyst increased with increase in the catalyst amount.

Temperature programmed oxidation (TPO) was conducted for the used samples. Figure 3 shows that the properties of the carbon deposited on the catalyst are dependent on the catalyst amount. Two peaks with 50 mg of catalysts appeared at 380 °C and at 662 °C in TPO. The intensity of the peaks appeared below 550 °C increased with increase in the catalyst amount. The peak at 662 °C can be assigned to the graphitic carbon.²⁸

The graphitic carbon was regarded to be inactive and thus

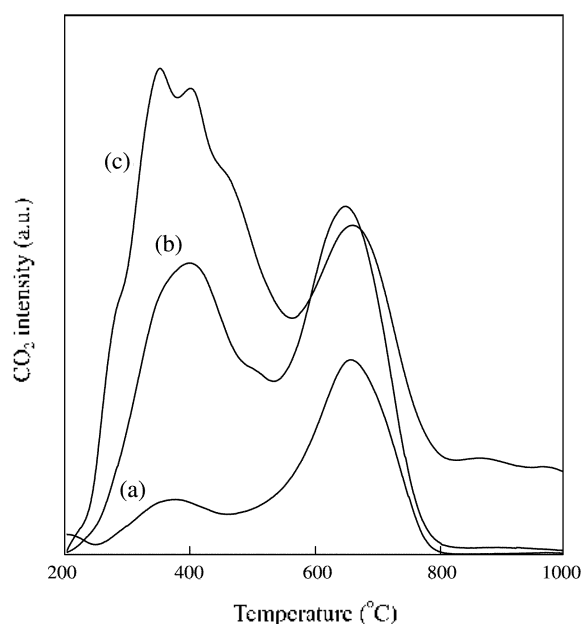


Figure 3. TPO analysis of the used catalysts after CO₂ reforming of methane at 750 °C for 16 h with different catalyst amounts: (a) 50 mg, (b) 100 mg, (c) 200 mg.

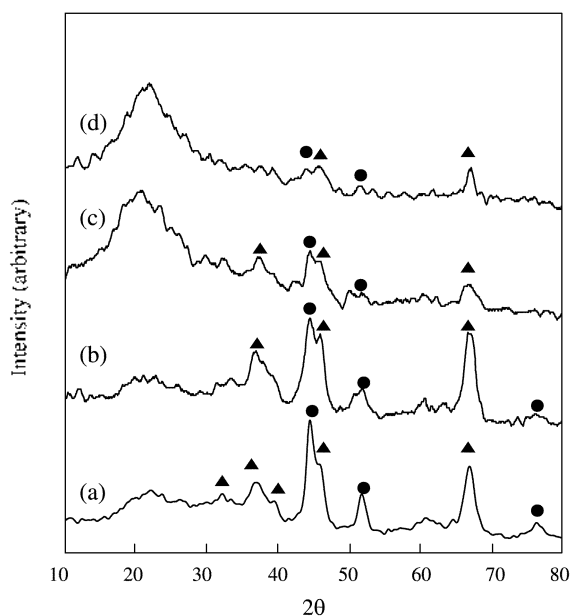
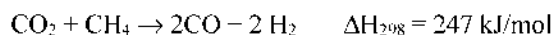


Figure 4. XRD spectra of (a) the fresh reduced catalyst and the used catalyst samples at 750 °C for 16 h with the amount of (b) 50 mg, (c) 100 mg, (d) 200 mg; (▲) γ -Al₂O₃, (●) Ni metal.

responsible for the deactivation, while the carbonaceous species combustible at the temperature below 550 °C is considered to be reversibly converted to CO by CO₂ oxidation.^{28,29} That is, the carbonaceous species combustible below 550 °C can be converted to CO with CO₂ by the reverse Boudouard reaction ($C + CO_2 \rightarrow 2 CO$). Therefore, the conversion of the carbonaceous species to CO with CO₂ decreases with lowering of the reaction temperature. TPO experiments with the used samples at the different temperatures showed that the carbonaceous species combustible below 550 °C increased with a decrease in the reaction temperature.²⁹ CO₂ reforming reaction is highly endothermic.



Therefore, it is highly probable that the temperature of the catalyst surface could be severely lowered by the endothermic reaction. The conversion of the carbonaceous species to CO with CO₂ below 550 °C could be suppressed due to lowering of the reaction temperature, resulting in the accumulation of a large amount of carbonaceous species.

Figure 4 shows XRD spectra for the three samples (50 mg, 100 mg, 200 mg) after 16 h reaction. The peak around 26° can be assigned to the graphitic carbon. Interestingly, the broad peak around 21° increased with increasing the amount of the catalyst, which can be assigned to the carbonaceous species combustible below 550 °C in the TPO experiments. The intensity of the characteristic peaks of γ -Al₂O₃ and Ni metal was severely decreased by the carbon deposition, indicating that the surface of γ -Al₂O₃ and Ni metal could be covered by the carbonaceous species. The characteristic peaks of Ni metal decreased more rapidly than that of γ -Al₂O₃, suggesting that the carbonaceous species covered mainly the surface of Ni metal.

Figure 5 shows TEM images of the samples of 50 mg and 200 mg after the reaction. The size of Ni crystallite in both TEM images was distributed with an average particle size of 50 nm. The carbon tubes with the diameter of 20-100 nm were observed on the sample of 200 mg, but it was not observed on that of 50 mg. It is interesting to observe that the carbon tubes could be formed with the increase of the carbonaceous species combustible below 550 °C in TPO. TEM images with the sample of 200 mg shows more clear black spot than that that with 50 mg. Nickel particles in TEM images with the sample of 200 mg seem to be segregated from the support, indicating that nickel particle can be detached from the support during carbon tube formation. At this moment, it is not easy to elucidate the relation of the carbon tube growth and the accumulation of

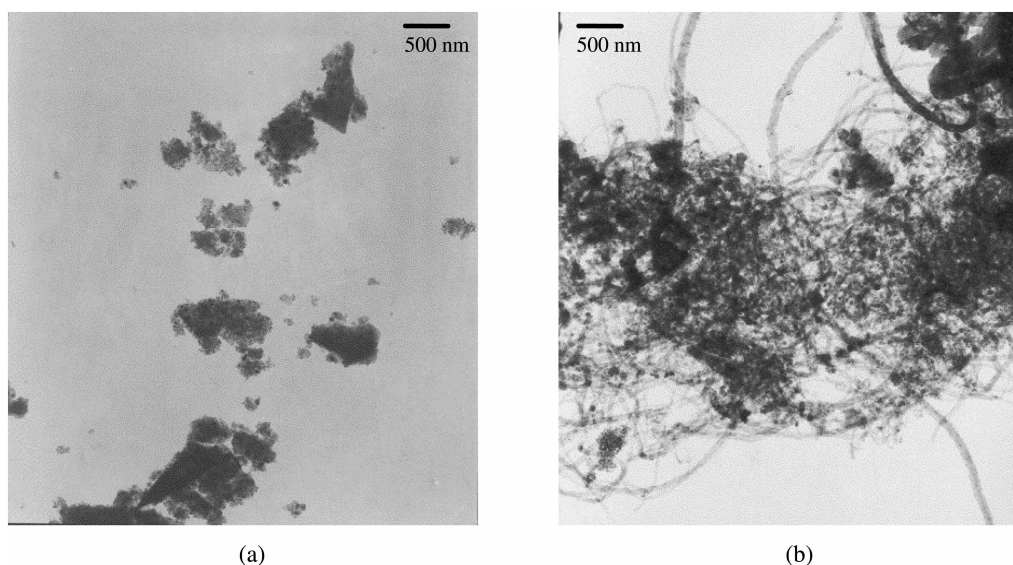


Figure 5. TEM images of the used catalysts at 750 °C for 16 h with the amount of (a) 50 mg, (b) 200 mg in 1/4" reactor.

the carbonaceous species combustible below 550 °C. However, the carbonaceous species below 550 °C seem to be related to carbon tube growth.

Conclusion

The conversion of CH₄ during CO₂ reforming of methane was dependent on the catalyst amount and the reactor size at the same temperature, pressure, and GHSV. TPO experiments with the samples after the CO₂ reforming of methane for 16h indicate that lowering of the catalyst bed temperature prevented the conversion of the carbonaceous species to CO with CO₂ by the reverse Boudouard reaction, resulting in the accumulation of the carbon on the catalyst, which was supported by XRD and TEM experiments. It can be concluded that the carbon deposition in the reactor with increase of the catalyst amount could be due to the accumulation of the carbonaceous species combustible below 550 °C in TPO experiment rather than to the formation of graphitic carbon.

References

- Vannice, M. A. *Catal. Rev.* **1976**, *14*, 153.
- Ross, J. R. H.; van Keulen A. N. J.; Hegarty, M. E. S.; Seshan, K. *Catal. Today* **1996**, *30*, 193.
- Gadalla, A. M.; Bower, B. *Chem. Eng. Sci.* **1988**, *43*, 3049.
- Hansen, J. B.; Voss, B.; Joensen, F.; Sigurdardottir, I. D. *SAE Paper 950063*, 1995.
- Jung, K. D.; Joo, O. S. *NICE* **2002**, 1.
- Kong, S. J.; Chung, T. S.; Lee, S. J.; Yoon, K. J. *HWAHAK KONGHAK* **2002**, *40*(1), 16.
- Moon, K. I.; Kim, C. H.; Choi, J. S.; Lee, S. H.; Kim, Y. G.; Lee, J. S. *HWAHAK KONGHAK* **1997**, *35*(6), 883.
- Inui, T.; Ichino, K.; Matsuoka, I.; Takeguchi, T.; Iwamoto, S.; Pu, S. B.; Nishimoto, S. *Korean J. Chem. Eng.* **1997**, *14*(6), 441.
- Vernon, P. D. F.; Green, M. L. H.; Cheetham, A. K.; Ashcroft, A. T. *Catal. Today* **1992**, *13*, 47.
- Edwards, J. H.; Do, K. T.; Maitra, A. H.; Schuck, S.; Stein, W. *Sol. Eng.* **1995**, *1*, 389.
- Ashcroft, T.; Cheetham, A. K.; Green, M. L. H.; Vernon, P. D. F. *Nature* **1991**, *352*, 225.
- Bitter, J. H.; Hally, W.; Seshan, K.; van Ommen, J. G.; Lercher, J. A. *Catal. Today* **1996**, *29*, 349.
- Choudhary, V. R.; Uphade, B. S.; Mamman, A. S. *Catal. Lett.* **1995**, *32*, 387.
- Bradford, M. C. J.; Vannice, M. A. *Appl. Catal. A* **1996**, *142*, 97.
- Wei, J.; Xu, B.; Li, J.; Cheng, Z.; Zhu, Q. *Appl. Catal. A* **2000**, *196*, 16.
- Zhang, Z.; Verykios, E. *Appl. Catal. A* **1996**, *138*, 109.
- Hu, Y. H.; Ruckenstein, E. *Catal. Rev.* **2002**, *44*(3), 423.
- Ruckenstein, E.; Hu, Y. H. *Appl. Catal.* **1997**, *43*, 71.
- Rostrup-Nielsen, J. R. *J. Catal.* **1984**, *85*, 31.
- Wang, S.; Lu, G. Q. *Applied Catalysis B* **1998**, *19*, 267.
- Montoya, J. A.; Romero-Pascual, E.; Gimon, C.; Angel, P. D.; Monzón, A. *Catalysis Today* **2002**, *63*, 71.
- Roh, H. S.; Jun, K. W.; Paek, S. C.; Park, S. E. *Catal. Lett.* **2002**, *81*, 147.
- Seok, S. H.; Choi, S. H.; Park, E. D.; Han, S. H.; Lee, J. S. *J. Catal.* **2002**, *209*, 6.
- Swaan, H. M.; Kroll, V. C. H.; Martin, G. A.; Mirodatos, C. *Catal. Today* **1994**, *21*, 571.
- Joo, O. S.; Jung, K. D. *Bull. Korean Chem. Soc.* **2002**, *23*(8), 1149.
- Olsbye, U.; Moen, O.; Slagtern, A.; Dahl, I. M. *Appl. Catal.* **2002**, *228*, 289.
- Wurzel, T.; Malcus, S.; Mleczko, L. *Chem. Eng. Sci.* **2000**, *55*(18), 3955.
- Wang, S.; Lu, G. Q. *Ind. Eng. Chem. Res.* **1999**, *38*, 2615.
- Zhang, Z. L.; Verykios, X. E. *Catal. Today* **1994**, *21*, 589.