

## CH<sub>4</sub> Dry Reforming on Alumina-Supported Nickel Catalyst

Oh-Shim Joo\* and Kwang-Deog Jung

*Eco-Nano Research Center, Korea Institute of Science and Technology,  
Cheongryang P.O. Box 131, Seoul 130-650, Korea*

*Received April 9, 2002*

CH<sub>4</sub>/CO<sub>2</sub> dry reforming was carried out to make syn gas on the Ni/Al<sub>2</sub>O<sub>3</sub> catalysts calcined at different temperatures. The Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst gave good activity and stability whereas the Ni/Al<sub>2</sub>O<sub>3</sub> (450 °C) catalyst showed lower activity and stability. The NiO/Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 850 °C for 16 h (Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C)) formed the spinel structure of nickel aluminate, which was confirmed by TPR. The carbon formation rate on the Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst was very low till 20 h, and then steeply increased with reaction time without decreasing the activity for CH<sub>4</sub> reforming. The Ni/Al<sub>2</sub>O<sub>3</sub> (450 °C) catalyst showed high carbon formation rate at the initial reaction time and then, the rate nearly stopped with continuous decreasing the activity for CH<sub>4</sub> reforming. Even though the amount of carbon deposition on the Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst was higher than that on the Ni/Al<sub>2</sub>O<sub>3</sub> (450 °C) catalyst, the activity for CH<sub>4</sub> reforming was also high, which could be attributed to the different type of the carbon formed on the catalyst surface.

**Key words :** Methane, Carbon dioxide, Dry reforming, Nickel aluminate, Carbon deposition

### Introduction

The catalytic CH<sub>4</sub> reforming with CO<sub>2</sub>, in which the mixture gas could be converted into synthesis gas of a low H<sub>2</sub>/CO ratio of 1, has been extensively examined for the past few decades.<sup>1-5</sup> The synthesis gas is suitable for the Fischer Tropsch Synthesis and the direct production of dimethyl ether (DME). The nickel metal is catalytically active for the reforming reaction, but excess carbon deposition on the metal surface causes the catalyst deactivation.<sup>6-10</sup> The deactivation prevents the nickel catalyst from the commercialization for the CH<sub>4</sub> reforming. Although noble metals have been proved to be less sensitive for carbon deposition on the surface,<sup>11,12</sup> it is important to develop Ni-based catalyst because of low cost and high availability of the nickel. Therefore, much attention has been focused on the development for Ni-based catalysts doping alkali metal or metal oxide as well as changing supports, suppressing the carbon deposition.<sup>1,13-14</sup> The origin of deposited carbon may be via CH<sub>4</sub> decomposition and CO disproportionation in the CH<sub>4</sub> reforming with CO<sub>2</sub>. Carbon deposition in reforming reaction may be closely related to the active catalyst structure. It has been known that the nickel aluminate could be formed during the calcination step of alumina supported-Ni catalyst.<sup>15-17</sup> Chen and Ren<sup>18</sup> also reported that the NiAl<sub>2</sub>O<sub>4</sub> spinel formed during preparation of the nickel catalyst could markedly reduce the carbon deposition in the reforming reaction. It has been reported that the reduction of the nickel aluminate would result in the formation of small nickel particles which are resistant to sintering and carbon formation.<sup>19</sup>

The goal of this paper is to observe the effect of

calcination temperature on the catalytic activity and stability of the Ni/Al<sub>2</sub>O<sub>3</sub> (450 or 850 °C) catalysts. For the purpose, the CH<sub>4</sub> dry reforming reaction was performed in a quartz reactor and the amount of carbon deposited was also determined in a Cahn Balance reactor with reaction time. It was found that besides the amount of the carbon deposition, the catalyst deactivation occurred on the Ni/Al<sub>2</sub>O<sub>3</sub> (450 °C) catalysts.

### Experimental Section

The alumina (Harshaw, Al-4183, 173.4 m<sup>2</sup>/g) supported 2.5 wt% Ni catalysts were prepared by the impregnation with aqueous solutions of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, followed by overnight drying at 120 °C in a vacuum oven and then, by calcination in a furnace at 450, 650, and 850 °C for 16 h. The calcination temperatures were denoted as NiO/Al<sub>2</sub>O<sub>3</sub> (450 or 850 °C) in parentheses. The calcined catalysts were reduced at 850 °C for 2 h before reaction, which were described in the form of Ni/Al<sub>2</sub>O<sub>3</sub> (450 or 850 °C). Nickel aluminate was prepared by the co-precipitation to confirm the NiAl<sub>2</sub>O<sub>4</sub> phase by TPR<sup>20</sup> and the precursor was calcined at 1000 °C for 5 h. The 33.2 wt% nickel aluminate of a distinct blue color was obtained.

The CH<sub>4</sub> dry reforming with CO<sub>2</sub> was carried out in a quartz (O.D. 3/8") and in a Cahn Balance (Cahn C2000 Electrobalance) reactor at the atmosphere pressure with the CO<sub>2</sub>/CH<sub>4</sub> ratio of 1.2 in the reactant gas. The feed rate of the reactant was 12,000 cc/g<sub>cat</sub>·h and the amount of catalyst was 100 mg. The exit gas for the quartz reactor was monitored with a gas chromatograph (Shimadzu 8A instrument with a TCD and Porapak T column 1/8" O.D., 3 m long in program temperature mode for separating N<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>O). The weight change of the Ni/Al<sub>2</sub>O<sub>3</sub> (450 or 850 °C) catalysts during the reforming reaction was monitored in a

\*Corresponding Author. Phone: +82-2-958-5215, Fax: +82-2-958-5219, E-mail: jooocat@kist.re.kr

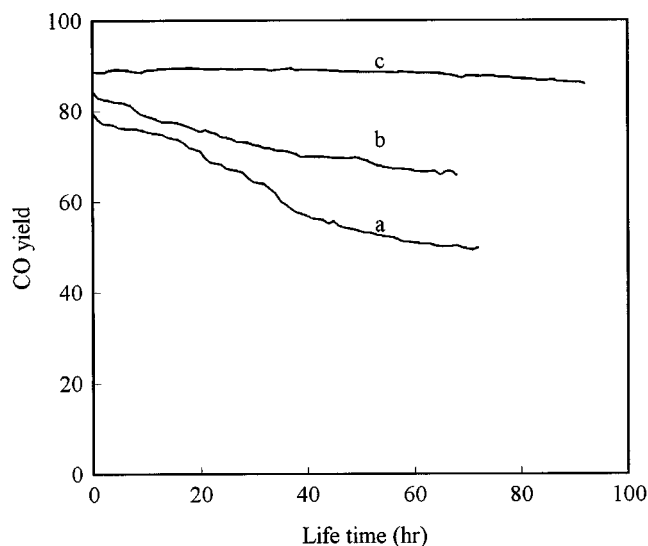
Cahn balance reactor for 70 h, and then TGA (Thermal Gravimetric Analysis) was carried out at the heating rate of 10 K/min and the flow rate of 30 mL/min of 3% O<sub>2</sub> in argon. A quadrupole mass spectrometer (Balzers, MS-Cube 200) was used to analyze the product components during CH<sub>4</sub> reforming and TGA in the Cahn balance reactor. For the detection of O<sub>2</sub>, CO, and CO<sub>2</sub> with the oxidation time, the intensities at *m/e* = 32, 28, 44 were monitored, respectively.

The catalysts were also characterized using TPR and TEM. The reducibility of the NiO/Al<sub>2</sub>O<sub>3</sub> (450 or 850 °C) and nickel aluminate was investigated by a temperature-programmed reduction (TPR), which was carried out at the heating rate of 10 K/min and the flow rate of 50 mL/min of 5% H<sub>2</sub> in argon. The hydrogen consumption for the reduction was monitored by a TCD. 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.

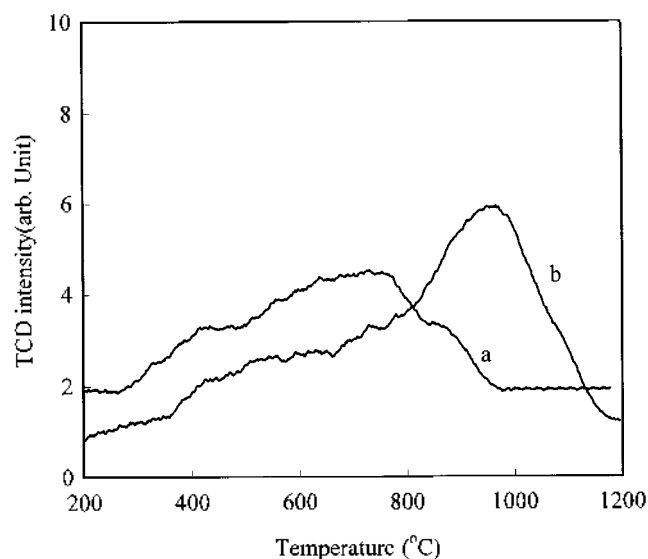
### Results and Discussion

CH<sub>4</sub> dry reforming with CO<sub>2</sub> was performed on the Ni/Al<sub>2</sub>O<sub>3</sub> catalysts at 750 °C to observe the effect of calcination temperature on the activity and stability of the reaction. The influence of the calcination temperature on the CO yield with reaction time was shown in Figure 1. The Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst showed the highest activity and stability whereas the Ni/Al<sub>2</sub>O<sub>3</sub> (450 °C) catalyst gave lowest activity and stability at the same reaction temperature of 750 °C. The activity of the Ni/Al<sub>2</sub>O<sub>3</sub> (450 or 650 °C) catalysts continuously decreased with reaction time. It meant that the calcination of the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst at different temperature changed the property of the catalyst, causing the different activity and stability of the catalysts.

The reducibility of the NiO/Al<sub>2</sub>O<sub>3</sub> (450 or 850 °C) catalyst was monitored by TPR. Figure 2 indicated the TPR spectra of the catalysts. The T<sub>max</sub> peak for the reduction of the NiO/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst appeared around 950 °C whereas the peak for the NiO/Al<sub>2</sub>O<sub>3</sub> (450 °C) catalyst was around 700 °C. The results showed that there was some different behavior depending on the calcination temperature. It has been examined that the NiO with Al<sub>2</sub>O<sub>3</sub> could be transformed into NiAl<sub>2</sub>O<sub>4</sub> spinel structure during heat treatment at high temperature.<sup>15-17</sup> The existence of nickel aluminate phase in the NiO/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst was confirmed by TPR. The reduction spectra of NiO, NiO/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst, and nickel aluminate prepared by co-precipitation were indicated in Figure 3. Only NiO could be reduced around 450 °C, but NiO/Al<sub>2</sub>O<sub>3</sub> (850 °C) and nickel aluminate were reduced around 950 °C. The T<sub>max</sub> peak for the reduction of NiO/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst was mostly identical with that of nickel aluminate. The result meant that the NiO on the alumina support was transformed into nickel aluminate phase with calcination at 850 °C for 16 h. Scheffer *et al.*<sup>15</sup> identified different nickel species in an alumina supported catalyst, based on the temperature range in which the species were reduced. According to the result, the nickel aluminate



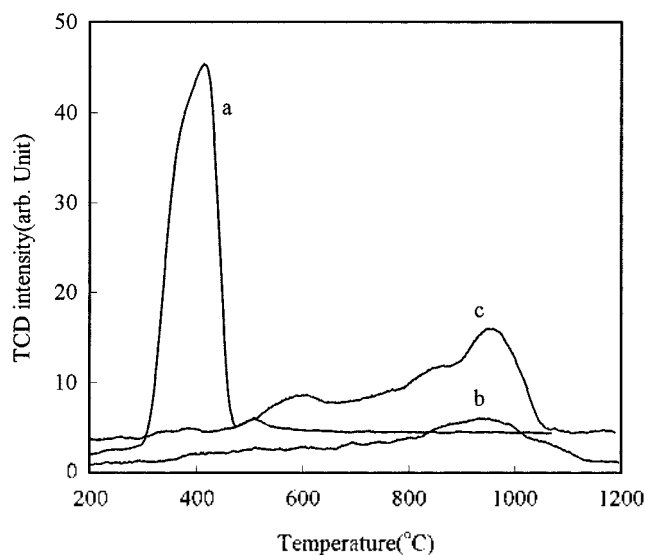
**Figure 1.** CO Yield on the Ni/Al<sub>2</sub>O<sub>3</sub> (450, 650 or 850 °C) catalysts at 750 °C. Calcination temperature: (a) 450 °C; (b) 650 °C; (c) 850 °C, GHSV = 12,000, CO<sub>2</sub>/CH<sub>4</sub> = 1.2, W<sub>cat</sub> = 100 mg.



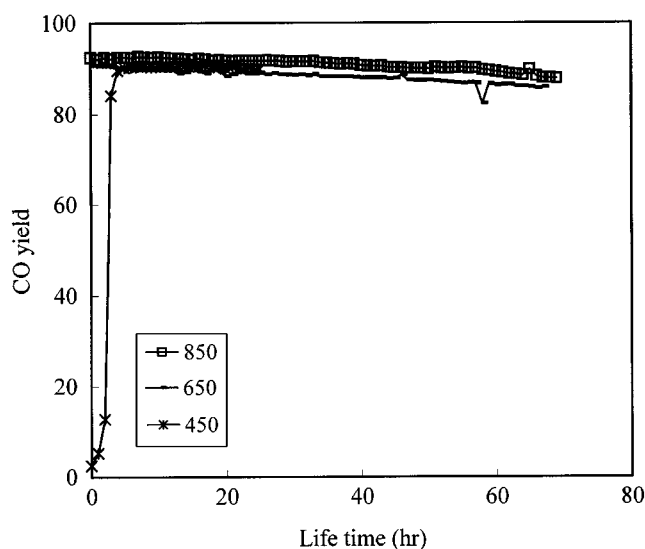
**Figure 2.** TPR spectra of the NiO/Al<sub>2</sub>O<sub>3</sub> (450 or 850 °C) catalysts: Calcination temperature: (a) 450 °C; (b) 850 °C, the flowrate of 5% H<sub>2</sub> = 60 cc/min, heating rate = 20 K/min.

was reduced up to 1000 °C. It is interesting to note that the Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst showed good activity and stability as shown in Figure 1.

The NiO/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst did not show any activity for the CH<sub>4</sub> dry reforming with CO<sub>2</sub> even at 750 °C. Therefore, the CH<sub>4</sub> reforming reaction was carried out at 750 °C to confirm the activity of the Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) depending on the reduction temperature. The catalysts were reduced at each temperature of 450, 650, and 850 °C for 2 h just before starting the reaction. The Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst reduced at 650 or 850 °C gave almost the same activity and stability, but the catalyst reduced at 450 °C gave very low activity at initial reaction time as shown in Figure 4. It nearly took 5 h to reach toward the activity of the Ni/



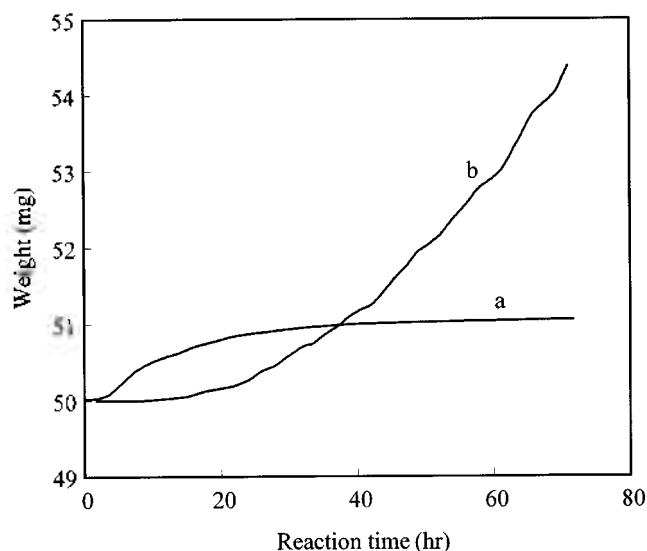
**Figure 3.** TPR spectra of NiO, nickel aluminate, and NiO/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst: (a) NiO (30 mg); (b) NiO/Al<sub>2</sub>O<sub>3</sub> (850 °C, 150 mg); (c) Nickel aluminate (100 mg), the flowrate of 5% H<sub>2</sub> = 60 cc/min, heating rate = 20 K/min.



**Figure 4.** CO Yield on the Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalysts depending on the reduction temperature: GHSV = 12,000, CO<sub>2</sub>/CH<sub>4</sub> = 1.2, W<sub>cat</sub> = 100 mg, RT = 750 °C, Reduction for 2 h.

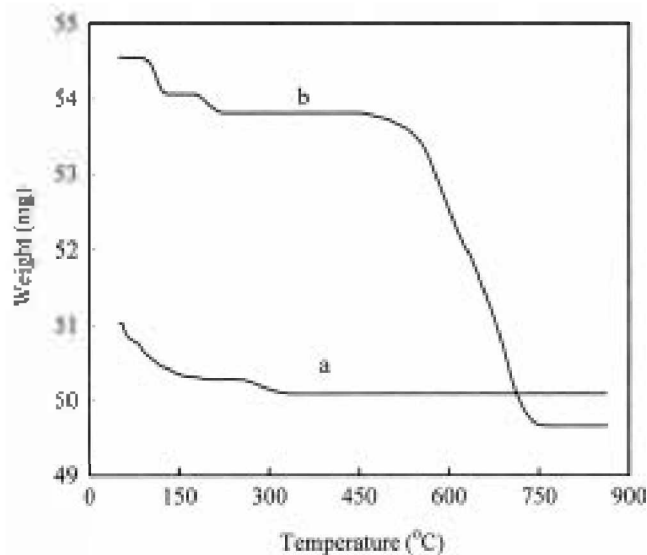
Al<sub>2</sub>O<sub>3</sub> (850 °C) catalysts reduced at 650 or 850 °C. The Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst reduced at 450 °C for 2 h could be not reduced enough into the nickel metal so the catalysts rarely showed activity at the initial reaction time. The catalyst might be slowly reduced under the atmosphere of CO and H<sub>2</sub> during the reforming reaction and then, became active. The activity and the stability of the Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalysts was not dependant on the reduction temperature as long as the catalyst was reduced. The nickel aluminate did not show any activity unless the catalysts were reduced. It indicated that the nickel metal could be an active component for the CH<sub>4</sub> reforming.

The carbon deposition on the nickel catalyst surface has

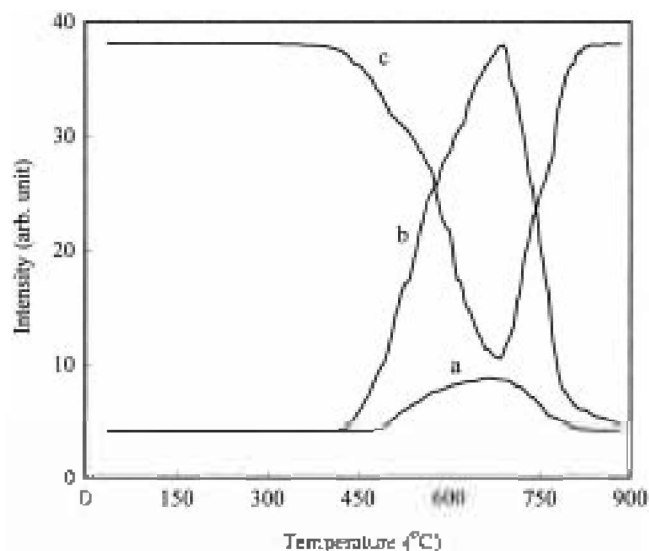


**Figure 5.** Weight increase on the Ni/Al<sub>2</sub>O<sub>3</sub> (450 or 850 °C) catalysts during reforming reaction for 70 h at 750 °C: (a) Ni/Al<sub>2</sub>O<sub>3</sub> (450 °C); (b) Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C), GHSV = 12,000, CO<sub>2</sub>/CH<sub>4</sub> = 1.2, W<sub>cat</sub> = 50 mg.

been well known for the deactivation of CH<sub>4</sub> dry reforming. The CH<sub>4</sub> reforming on the Ni/Al<sub>2</sub>O<sub>3</sub> (450 or 850 °C) catalysts was carried out in a Cahn Balance reactor at the reaction temperature of 750 °C to directly measure the amount of the carbon deposited during the reaction. The weight increase on the catalyst with the reaction time was shown in Figure 5. The pattern of the weight increment was so different on the Ni/Al<sub>2</sub>O<sub>3</sub> (450 or 850 °C) catalysts, which was dependant on the calcination temperature of the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. The weight increase rate on the Ni/Al<sub>2</sub>O<sub>3</sub> (450 °C) catalyst was high at the initial reaction time, and then gradually decreased and then, leveled off after 10 h. On



**Figure 6.** Weight decrease on the Ni/Al<sub>2</sub>O<sub>3</sub> (450 or 850 °C) catalysts by oxidation after reaction for 70 h at 750 °C: (a) Ni/Al<sub>2</sub>O<sub>3</sub> (450 °C); (b) Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C).

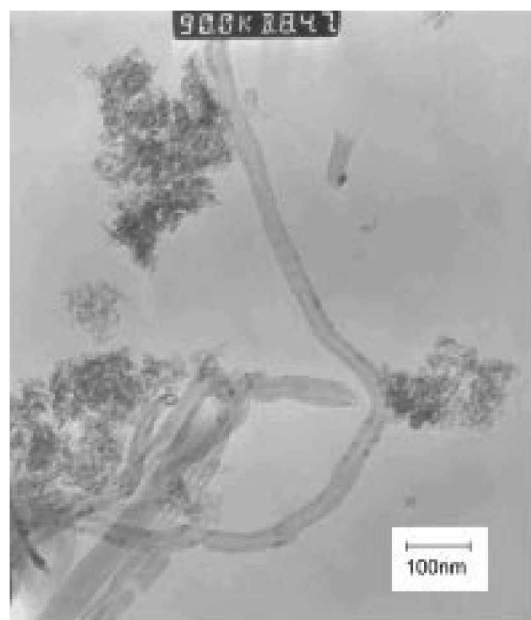


**Figure 7.** TPO spectra of the Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst after reaction for 70 h: (a) CO; (b) CO<sub>2</sub>; (c) 3% O<sub>2</sub> in balance of argon.

the other hand, the weight increase rate on the Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst until 20 h was almost zero, and then the rate steeply increased during the reforming reaction. The weight increase came from the carbon deposition on the catalyst surface during the reforming reaction. Although the amount of carbon deposition on the Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst was high, the catalyst kept high activity with reaction time as shown Figure 1. But, the activity of the Ni/Al<sub>2</sub>O<sub>3</sub> (450 °C) catalyst gradually decreased with reaction time, even though the carbon deposition was almost stopped after 10 h. It suggested that the deactivation of the Ni/Al<sub>2</sub>O<sub>3</sub> (450 °C) catalyst probably is related to the type carbon deposited rather than the amounts of the carbon deposited.

After the CH<sub>4</sub> reforming for 70 h, the used catalysts in the Cahn balance reactor were oxidized at the heating rate of 10 K/min and the flow rate of 30 mL/min with 3% O<sub>2</sub> in argon. The weight decrease on the Ni/Al<sub>2</sub>O<sub>3</sub> (450 or 850 °C) catalyst during the TGA was shown in Figure 6. The exit gas was monitored by a quadrupole mass spectrometer (Balzers, MS-Cube 200) to analyze the product components during the TGA. The spectra for the O<sub>2</sub>, CO, and CO<sub>2</sub> with the oxidation temperature during the TGA were depicted in Figure 7. The carbon on the catalyst surface was oxidized mostly into CO<sub>2</sub> and partly into CO.

The carbon on the Ni/Al<sub>2</sub>O<sub>3</sub> (450 °C) catalyst was mostly oxidized at the temperature under 300 °C, but the most carbon on the Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst was oxidized at the temperature above 500 °C. The difference of the oxidation temperature indicated that the carbon type formed on the catalyst surface was so different depending on the calcination temperature of the catalyst. The carbon formed on the Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst might be the carbon having long-range order than that on the Ni/Al<sub>2</sub>O<sub>3</sub> (450 °C) catalyst. The carbon having long-range order would be oxidized at a higher temperature. The carbon nanotube grown over 0.5 wt% Ni-Fe/Al<sub>2</sub>O<sub>3</sub> from the dehydrogenation of ethylene



(a)



(b)

**Figure 8.** TEM image for the used catalysts of Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C): (a) and Ni/Al<sub>2</sub>O<sub>3</sub> (450 °C): (b).

(C<sub>2</sub>H<sub>4</sub>) at 750 °C was oxidized at the same temperature range.<sup>21</sup> The carbon nanotube had much long-range order than amorphous carbon.<sup>22</sup>

Generally, it has been proposed that carbon deposition on a catalyst surface induce the catalyst deactivation. But, the Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst gave the high activity and stability, although the catalyst showed the much amount of carbon deposition during the CH<sub>4</sub> reforming. Whereas, the Ni/Al<sub>2</sub>O<sub>3</sub> (450 °C) catalyst showed lower activity and stability as shown in the Figure 1, although the small amount of carbon formed on the catalyst. According to the results, it is important to mention that the amount of carbon deposition

was not always related to the catalyst deactivation. Chen and Ren<sup>18</sup> reported that the carbon deposition on the NiAl<sub>2</sub>O<sub>4</sub> spinel was markedly suppressed during the CH<sub>4</sub> reforming reaction. Their results were correctly agreed with our results during the reaction time till around 30 h in which the carbon deposition on the Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst was strongly suppressed, whereas increased on the Ni/Al<sub>2</sub>O<sub>3</sub> (450 °C) catalyst. Moreover, the Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst showed high stability, whereas the Ni/Al<sub>2</sub>O<sub>3</sub> (450 °C) catalyst showed low stability. It suggested that the controversial results on the relationship of the amount of carbon with the activity and stability could come according to the analysis point for the amount of carbon deposited.

TEM images were taken for the used Ni/Al<sub>2</sub>O<sub>3</sub> (450 or 850 °C) catalysts after 70 h reactions to discriminate the type of the carbon and the metal particle size. The TEM image for the used catalysts was shown in Figure 8. The Ni/Al<sub>2</sub>O<sub>3</sub> (450 °C) catalyst consisted of large metal particle in comparison to the Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst as shown in the Figure 8. The amorphous carbon on the Ni/Al<sub>2</sub>O<sub>3</sub> (450 °C) catalyst covered nearly all the catalyst surfaces (the black part of the TEM image), which could result in the decrease in the catalytic activity with the reaction time. Therefore, the stability of the catalyst decreased with reaction time, even though the amount of carbon deposition was small on the Ni/Al<sub>2</sub>O<sub>3</sub> (450 °C) catalyst. On the other hand, there was no amorphous type carbon on the Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst, showing only the filament type carbon. Therefore, most active metal could be exposed to the reactants during the reaction, even though the amount of the carbon deposition was steeply increased after 20 h. As shown in the Figure 8, most of the carbon was the filament type, not covering the catalyst surface.

The carbon deposited on an active metal surface could be a serious reason on the catalyst deactivation for the CH<sub>4</sub> dry reforming with CO<sub>2</sub>. Rostrup-Nielsen J.R. reported that large metal particles stimulated the amorphous carbon deposition because of ensemble effect,<sup>23</sup> which was covering the active metal surface. On the other hand, the growth of a filament carbon occurs on a metal surface in which the active metal is carried on the top of the filament carbon.<sup>24-27</sup> The filament carbon deposition could keep the catalytic activity with reaction time because the active metal was still exposed to the reactants in the case of filament carbon formation on an active catalyst surface.

The nickel aluminate in the Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst was reduced into small size Ni metal than in the Ni/Al<sub>2</sub>O<sub>3</sub> (450 °C) catalyst, which might give high activity and stability for the CH<sub>4</sub> reforming.

### Conclusions

The activity and stability of the 2.5 wt% Ni/Al<sub>2</sub>O<sub>3</sub> (450 or 850 °C) catalysts for CH<sub>4</sub> reforming with CO<sub>2</sub> were tested depending on the calcination temperature. The NiO/Al<sub>2</sub>O<sub>3</sub>

(850 °C) catalyst consisted of nickel aluminate, which was not active for the reaction before reduction. The Ni/Al<sub>2</sub>O<sub>3</sub> (850 °C) catalyst showed good activity and stability for 70 h, although the amount of carbon deposition is higher than on the Ni/Al<sub>2</sub>O<sub>3</sub> (450 °C) catalyst. The phenomena might come from the different type of carbon formed on the catalysts during the CH<sub>4</sub> reforming. Amorphous carbon could cover all the active metal, but filament carbon was grown not covering the metal surface.

**Acknowledgment.** This research was performed for the clean energy technology development, funded by R&D Management Center for Energy and Resources of Korea Energy Management Corporation.

### References

- Jung, K. S.; Coh, B. Y.; Lee, H. I. *Bull. Korean Chem. Soc.* **1999**, *20*, 89.
- Wurzel, T.; Malcus, S.; Mleczko, I. *Chem. Eng. Sci.* **2000**, *55*, 3955.
- Wang, H. Y.; Ruckenstein, E. *Appl. Catal.* **2000**, *204*, 143.
- Luo, J. Z.; Yu, Z. L.; Ng, C. F.; Au, C. T. *J. Catal.* **2000**, *194*, 198.
- Tang, S.; Ji, L.; Zeng, H. C.; Tan, K. L.; Li, K. *J. Catal.* **2000**, *194*, 424.
- Zhang, Z. L.; Tsipouriani, Z. A.; Efsthioni, A. M.; Verykios, X. E. *J. Catal.* **1996**, *158*, 516.
- Ashcroft, A. T.; Cheetham, A. K.; Green, M. L. H.; Vernon, P. D. *Nature* **1991**, *352*, 225.
- Richardson, J. T.; Paripatyadar, S. A. *Appl. Catal.* **1990**, *61*, 293.
- Stagg, S. M.; Romeo, E.; Padro, C.; Resasco, D. E. *J. Catal.* **1998**, *178*, 137.
- Bitter, J. H.; Seshan, K.; Lercher, J. A. *J. Catal.* **1999**, *183*, 336.
- Bradford, M. C. J.; Vanniec, M. A. *J. Catal.* **1998**, *173*, 157.
- Tang, S.; Lin, J.; Tan, K. L. *Catal. Lett.* **1999**, *59*, 129.
- Osaki, T.; Mori, T. *J. Catal.* **2001**, *204*, 89.
- Kepinski, L.; Stasinska, B.; Borowiecki, T. *Carbon* **2000**, *38*, 1845.
- Scheffer, B.; Molhoek, P.; Moulijn, J. A. *Appl. Catal.* **1989**, *46*, 11.
- Arnoldy, P.; Moulijn, J. A. *J. Catal.* **1985**, *93*, 38.
- Mangnus, P. J.; Bos, A.; Moulijn, J. A. *J. Catal.* **1994**, *146*, 437.
- Chen, Y. G.; Ren, J. *Catal. Lett.* **1994**, *29*, 39.
- Bhattacharyya, A.; Chang, V. W. *Stud. Surf. Sci. Catal.* **1994**, *88*, 616.
- Srivastava, R. D.; Onuferko, J.; Schultz, J. M. *Ind. Eng. Chem. Fundam.* **1982**, *21*, 457.
- Kim, C. K.; Joo, O. S. unpublished results.
- Carbon Nanotubes: Preparation and Properties*, Ebbesen, T. W., Ed.; CRC Press, Inc.: 1997.
- Rostrup-Nielsen, J. R. In *Catalysis Science and Technology*; Springer-Verlag: Berlin, 1984; pp 1-118.
- Baird, T.; Fryer, J. R.; Grant, B. *Carbon* **1974**, *12*, 591.
- Baird, T.; Fryer, J. R.; Grant, B. *Nature* **1971**, *233*, 329.
- Baker, R. T. K.; Chludzinski, J. J.; Lund, C. R. F. In *Extended Abstracts of the 18<sup>th</sup> Biennial Conference on Carbon*, July 19-24, Worcester Polytechnic Institute: 1987; p 155.
- Tibbetts, G. G.; Devour, M. G.; Rodda, F. J. *Carbon* **1987**, *25*, 367.