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Carbon dioxide reforming of methane over Ni/Al_2O_3 treated with glow discharge plasma

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Abstract

Ni/Al_2O_3 catalyst was first treated by argon glow discharge plasma followed by calcination in air. The catalyst prepared this way exhibits an improved low-temperature activity for carbon dioxide reforming of methane, compared to the catalyst prepared without plasma treatment. The catalyst characterization using XRD, chemisorption and TEM analyses show that the plasma treatment followed by calcination thermally induces a generation of specific nickel species on the support. This kind of ''plasma'' metal species is highly dispersed on the support and can remain stable during reforming reactions. The average size of the ''plasma'' metal particles is ca. 5 nm. The plasma treatment can also enhance the anti-carbon deposition performance of the catalyst. The formation of carbon species that is responsible for catalyst deactivation can be inhibited. The catalyst stability is therefore improved.

Keywords: Methane; Reforming; Carbon dioxide; Ni/Al_2O_3; Pretreatment; Glow discharge

1. Introduction

Carbon dioxide reforming of methane to synthesis gas (syngas) has recently drawn a great attention. While it can convert the major undesirable greenhouse gases into valuable chemicals, a principal advantage of syngas production from CO_2 reforming is the low H_2/CO ratio obtained, which is suitable for further syntheses of valuable hydrocarbons [1,2]. It can be also applied directly for utilization of natural gas containing large amount of CO_2, without the pre-separation.

Numerous supported catalysts have been tested for CO_2 reforming. Among the catalysts tested, nickel and noble metal based catalysts have been found to exhibit promising catalytic performance [1–4]. Thermodynamically, high CO_2/CH_4 ratios (>1) and high temperatures are desired to minimize carbon formation in the CO_2 reforming of methane.

However, there is still no practical catalyst developed. Major problems associated with the application of CO_2 reforming of methane include the deactivation of catalysts due to the coke formation and sintering of catalyst suffered from high temperature reactions. In addition, high-energy input may induce an extra CO_2 emission for energy generation. It is desirable to operate the reaction at lower temperatures and with CO_2/CH_4 ratio near unity.

The catalysts based on noble metals are reported to be less sensitive to coking compared to nickel based catalysts [1–3]. However, these noble metals are expensive, which limits their application. Many investigators have devoted their effort towards the coke suppression in the case of nickel catalysts. It has been proved that the presence of modifiers [5–7] inhibits the coke formation. For example, addition of alkaline and alkaline earth metals to the catalyst was used to overcome the problem of coking with the Ni catalysts. Recently, the addition of a small amount of steam to the dry reforming feedstock [6–9] or a tri-reforming process [10–12] was reported in effort of eliminating the carbon formation.

Theoretically, controlling the size of the ensembles of metal atoms on the surface would be very helpful to inhibit carbon deposition. Previously reported studies confirmed that carbon deposition over Ni/Al_2O_3 depends on the catalyst structure, composition and preparation conditions [2].

The structure-sensitivity of carbon formation over Ni-containing catalysts provides the possibility for inhibition of the carbon deposition by the modification of the catalyst surface.

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Recently, we developed a novel plasma catalyst preparation technology, with which the catalyst is first treated by glow discharge plasma and then calcined thermally. A specific ‘‘plasma’’ metal cluster with typical structure and enhanced metal-support interaction can be formed this way [13]. A remarkable enhancement in the dispersion, low-temperature activity and stability has been obtained [14–16]. The reactions tested include methane combustion [14], NO reduction by methane [15] and partial oxidation of methane [16]. We have also attempted to use this method for the preparation of Ni/Al_2O_3 catalysts for carbon dioxide reforming of methane [17]. A strange low-temperature activity towards high selectivity of carbon deposit has been observed. During further investigations, we were very regretful to have found that the feed gas, carbon dioxide, applied previously was contaminated, which have induced a significant change in the reactions. In this work, we re-conduct the investigation with high purity CO_2, in order to confirm the effectiveness of the plasma catalyst preparation for CO_2 reforming.

2. Experimental

2.1. Catalyst preparation and test

The catalyst used in this work was prepared with the method as previously described [14–16]. The support Al_2O_3 was first impregnated by an aqueous solution of $Ni(NO_3)_2$ for ca. 12 h. The sample was then treated by glow discharge plasma. Fig. 1 shows the setup of the plasma treatment of Ni/Al_2O_3 powder. The discharge tube (i.d. 40 mm) was made of glass and the distance between the two electrodes was set at 100 mm. A dc high-voltage generator (made in Tianjin University) was used to generate glow discharge plasma. The catalyst powder was placed in the ‘‘positive column’’ of glow discharge that contains highly energetic electrons at low gas temperature. The glow discharge was initiated at room temperature in this work. Argon (>99.99% in purity) was applied as the plasma-forming gas. The gas temperature within the glow discharge was less than 40 °C, in terms of the temperature measurement using IR imaging. During the treatment, the pressure in the discharge tube was in the range of between 100 and 200 Pa. The applied voltage to the electrode was ca. 900 V. The voltage was measured with a high-voltage probe (Tektronix P6015A) via an oscilloscope (Tektronix TDS210). The discharge treatment time was 15 min and the treatment was repeated for three times in order to get a uniformly treated powder. After treatment by plasma, the catalyst was calcined at 600 °C for another 6 h in air and was then pressed, crushed and sieved to 40–60 meshes before reaction test.

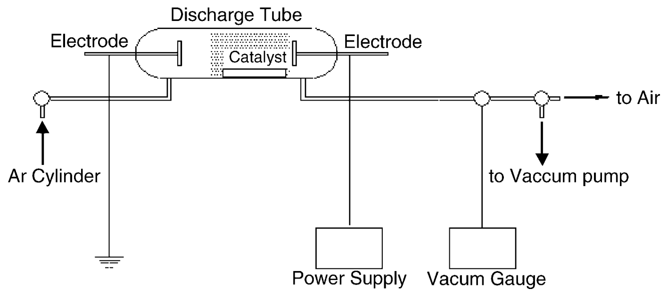

Fig. 1. The schematic representative of setup for glow discharge catalyst treatment.

The loading amount of nickel on the alumina support is 9 wt.%. The reaction of CO_2 reforming of methane was carried out at atmospheric pressure in a 6 mm i.d quartz-tube fixed-bed reactor. A thermocouple placed in the center of the catalyst bed was used to measure the reaction temperature. Before the reaction, the catalyst was reduced at 650 °C in flowing hydrogen at a flow rate of 50 ml/min for 2 h. Argon was used as the dilution gas during the reaction. The volume ratio of the feed gases was 1/1/2 of methane/carbon dioxide/argon. The total flow rate is 40 ml/min with a space velocity of 48,000 ml/h gcat. The effluents were analyzed using an online gas chromatography (Agilent 4890D) with a Porapak Q column. An ice-cold trap was used between the reactor exit and the GC sampling valve to remove the water formed during the reaction.

In this work, conversions of methane and carbon dioxide and selectivities of hydrogen and CO were calculated according to the following formulas:

$$X(\mathrm{CH_4})\% = \frac{(F_{\mathrm{CH_4,IN}} - F_{\mathrm{CH_4,OUT}})}{F_{\mathrm{CH_4,IN}}} \times 100$$

$$X(\mathrm{CO_2})\% = \frac{(F_{\mathrm{CO_2,IN}} - F_{\mathrm{CO_2,OUT}})}{F_{\mathrm{CO_2,IN}}} \times 100$$

$$S(\mathrm{H_2})\% = \frac{F_{\mathrm{H_2,OUT}}}{[2 \times (F_{\mathrm{CH_4,IN}} - F_{\mathrm{CH_4,OUT}})]} \times 100$$

$$S(\mathrm{CO})\% = \frac{F_{\mathrm{CO_2,OUT}}}{[(F_{\mathrm{CH_4,IN}} - F_{\mathrm{CH_4,OUT}}) + (F_{\mathrm{CO_2,IN}} - F_{\mathrm{CO_2,OUT}})]} \times 100$$

$$F_{\mathrm{i}} = C_{\mathrm{i}} \times F_{\mathrm{total}}$$

where X, S and F are conversion, selectivity and gas flow rate, respectively. F_{total} is the total feed rate or the gas effluent flow rate. C_{i} is the molar fraction of component i in the feed gas or in the gaseous effluent.

2.2. Catalyst characterization

The physisorption and chemisorption of catalysts was performed using a Quantachrome Autosorb-1-C Sorption system. The samples were degassed for 3 h at 350 °C before measurement. The Langmuir method was employed to calculate the surface areas, and BJH method for the average pore diameter. The specific nickel surface area was determined by CO chemisorption measurement. The samples were reduced at 600 °C in pure hydrogen with a flow rate of 30 ml/min for 1 h. The chemisorption measurements were carried out at 40 °C. The specific nickel surface area was calculated assuming a stoichiometric factor of 1 for the adsorption of CO on nickel atom by using Extrapolation method.

Table 1
Physisorption and chemisorption results of the support and the fresh catalyst

Catalysts	Langmuir surface area (m^2/g)	BJH average pore diameter (nm)	Active metal surface area (m^2/g)	Percent metal dispersion (%)	Average crystallite size (nm)
Al_2O_3	271.9	6.359	–	–	–
Ni/Al_2O_3	295.5	6.122	12.6	21.1	4.8

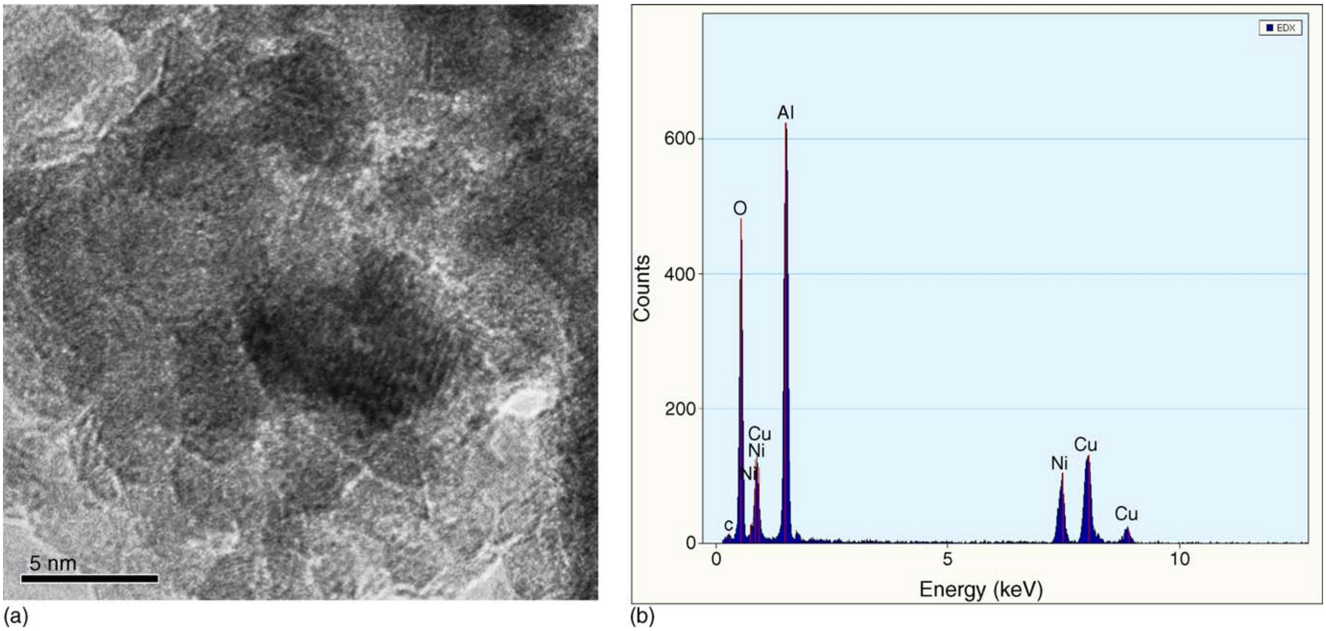

Fig. 2. (a) TEM image of fresh Ni/Al_2O_3; (b) EDX results.

X-ray powder diffraction (XRD) patterns of samples was recorded on an X' Pert Pro diffractometer using a Co Kα radiation at 40 kV and 40 mA with a scanning rate of 8°/min from $2\theta = 15–85°$.

Thermogravimetric analyses (TGA) were performed in a TA-50 thermal analyzer. N_2 (99.99%) and air (99.99%) at flow rates of 20 and 30 ml/min, respectively, were introduced into the instrument. Sample (ca. 10 mg) was loaded onto the thermo-balance and heated to 800 °C at a rate of 15 °C/min until a constant weight was obtained. The weight loss was recorded simultaneously.

TEM analysis was performed on a Tecnai G^2 F20 TEM apparatus for the fresh and used catalysts.

3. Results and discussion

3.1. Catalyst characterization

Table 1 presents the results of the physi-/chemisorption of Ni/Al_2O_3 catalyst. Obviously, a high dispersion of 21.1% of active metal Ni has been achieved over the plasma treated catalyst. The average crystallite size of nickel is below 5 nm.

Fig. 2(a) shows a TEM image of fresh catalyst. Some well-defined facets of Ni can be observed, confirmed by EDX analysis, as shown in Fig. 2(b).

It well known that there are three main peaks with XRD patterns of the conventionally prepared Ni/Al_2O_3 catalyst for carbon dioxide reforming of methane, defined as Ni, NiO and $NiAl_2O_4$ [18,19]. Fig. 3 exhibits the XRD patterns of the fresh plasma treated Ni/Al_2O_3 catalyst. A very interesting and surprising thing is that we cannot identify any peaks of Ni

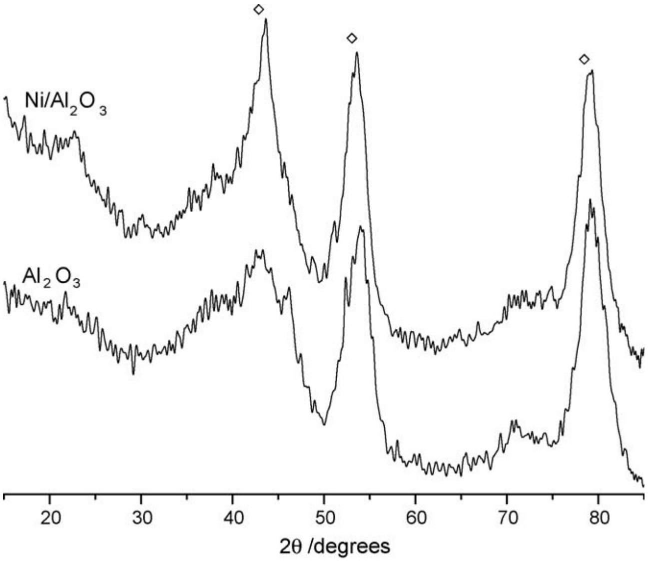

Fig. 3. XRD patterns of the support and fresh catalyst (◇): Al_2O_3.

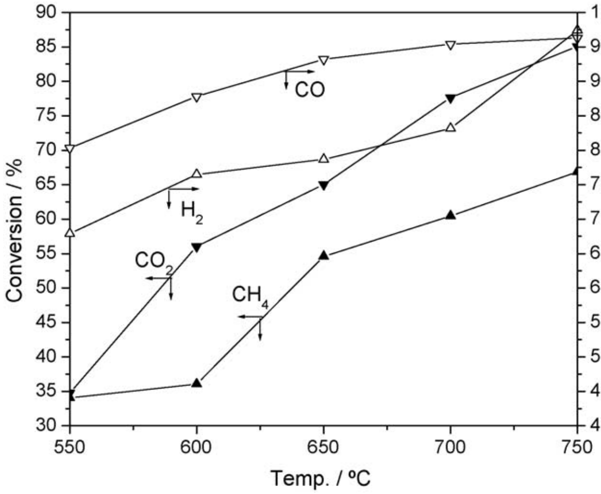

Fig. 4. The effect of temperature on the catalytic activity of Ni/Al_2O_3 (reaction condition: CH_4:CO_2:Ar = 10:10:20; space velocity = 48,000 ml/h gcat; Ni loading 9%).

species including Ni and NiO from the XRD patterns, even with a 9% nickel loading on the support! Only the alumina peaks are observed. This indicates that Ni particles were highly dispersed on the alumina support.

3.2. Catalytic activity

The effect of reaction temperature on catalytic activity is shown in Fig. 4. The conversions increase with the increasing reaction temperature. The CO_2 conversion is always higher than the CH_4 conversion. This suggests that the reverse water gas shift reaction occurs. Compared to the reported work, the present investigation demonstrates that the plasma treated catalyst possesses a better low-temperature activity. For example, compared to the reported work [20], methane conversion over the plasma treated catalyst has a 20% increase at the same reaction temperature (650 °C).

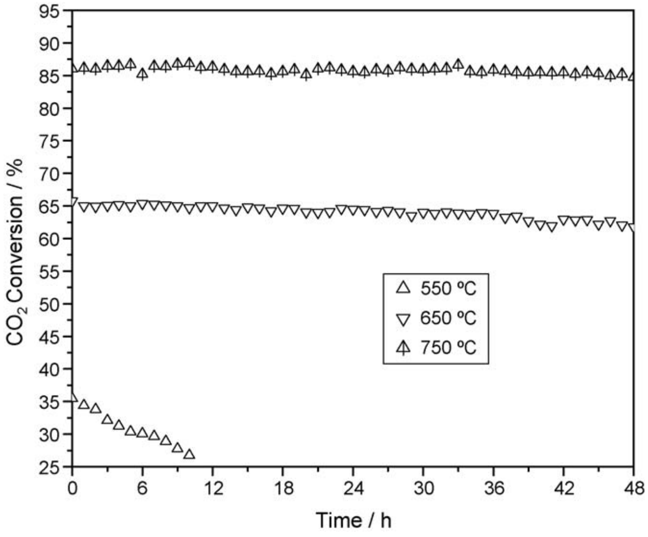

Fig. 6. The stability test represented by CO_2 conversion (reaction condition: CH_4:CO_2:Ar = 10:10:20; space velocity = 48,000 ml/h gcat; Ni loading 9%).

3.3. Stability

The stability tests were conducted at the temperatures of 550, 650 and 750 °C, respectively. The results are shown in Figs. 5–8. Evidently, the reaction temperature has a significant influence on the catalyst stability. At the reaction temperature of 550 °C, the catalyst shows a relatively faster deactivation. After 10-h reaction, the CH_4 and CO_2 conversions decrease from 32% and 36% to 20% and 26%, respectively. Similarly, CO and H_2 selectivities are reduced from 72% and 60% to 65% and 55%, respectively. At higher reaction temperatures (650 and 750 °C), the deactivation rates of catalysts are very slow. The coke formation is the main reason for the catalyst deactivation, especially at lower reaction temperatures. A relatively high reaction temperature is more kinetically favored for further coke conversion. At reaction temperatures of 650 and 750 °C, the plasma treated

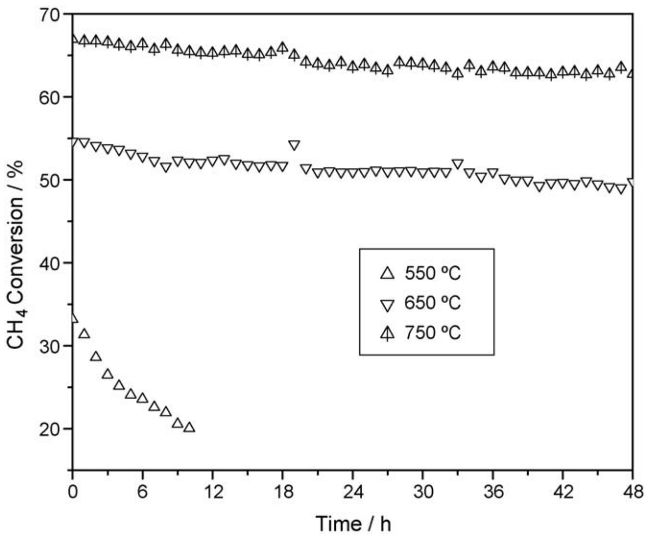

Fig. 5. The stability test represented by CH_4 conversion (reaction condition: CH_4:CO_2:Ar = 10:10:20; space velocity = 48,000 ml/h gcat; Ni loading 9%).

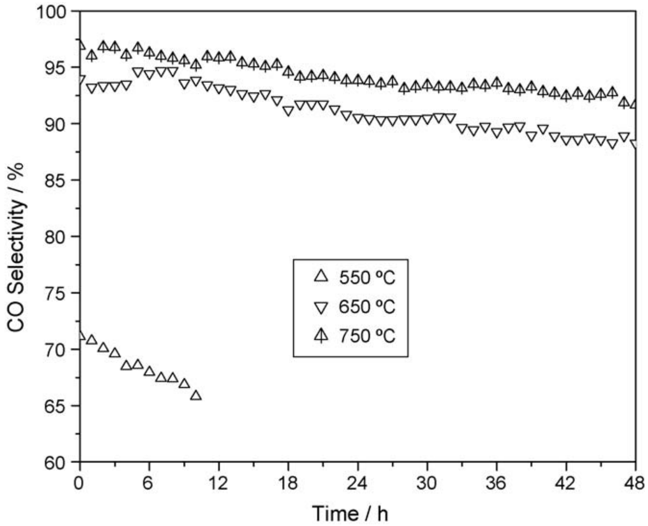

Fig. 7. The stability test represented by CO selectivity (reaction condition: CH_4:CO_2:Ar = 10:10:20; space velocity = 48,000 ml/h gcat; Ni loading 9%).

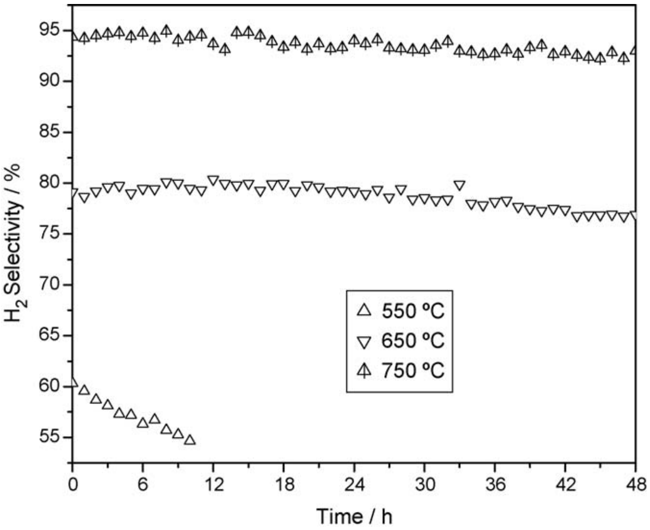

Fig. 8. The stability test represented by H_2 selectivity (reaction condition: CH_4:CO_2:Ar = 10:10:20; space velocity = 48,000 ml/h gcat; Ni loading 9%).

catalyst presents a very good stability, compared to the reported work.

Zhang et al. [21] reported that three kinds of carbonaceous species formed on the Ni/Al_2O_3 catalyst upon TGA analysis, designated as C_α at 150–220 °C, C_β at 530–600 °C, C_γ at >650 °C. At low reaction temperatures (500–600 °C), the catalyst surface is populated with the C_β species (whose amount corresponds to several monolayers of equivalent carbon on Ni crystallites), along with small amounts of the C_α species. However, the species C_β can change into the C_γ species when time of exposure is longer than 2 h. The active C_α species is responsible for formation of synthesis gas, while most of C_γ species is responsible for catalyst deactivation. The C_β species is a surface poison or spectator at low reaction temperature (<530 °C), but may participate in CO formation, to small extent, at high temperatures (>600 °C).

Table 2 presents the mass percentage of each carbonaceous species over the used plasma treated catalysts, calculated from TGA measurements. The total carbon amount formed on the used catalyst at reaction temperature of 550 °C is up to 9.34%, after only 10 h reaction. For catalysts used at 650 and 750 °C for 48 h, however, the amount is ca. 14%. It is interesting that only C_α and C_β carbonaceous species present on the used plasma treated catalysts. No C_γ species can be found. This means the plasma treatment can inhibit the formation of C_γ species. This suggests too that the glow discharge plasma treatment induces a significant change in the catalyst structure. Fig. 9 presents an example of the TGA analyses of used catalyst obtained with reaction temperature of 650 °C.

Table 2
The TGA analyses of used catalysts

Used catalysts	C_α (%)	C_β (%)	C_γ (%)	Total coke formation (%)
550 °C 10 h[a]	4.99	4.35	0	9.34
650 °C 48 h[b]	4.10	8.83	0	12.93
750 °C 48 h[c]	2.89	11.57	0	14.46

[a] Reaction temperature = 550 °C, CH_4/CO_2/Ar = 10/10/20, space velocity = 48,000 ml/h gcat, reaction time = 10 h.

[b] Reaction temperature = 650 °C, CH_4/CO_2/Ar = 10/10/20, space velocity = 48,000 ml/h gcat, reaction time = 48 h.

[c] Reaction temperature = 750 °C, CH_4/CO_2/Ar = 10/10/20, space velocity = 48,000 ml/h gcat, reaction time = 48 h.

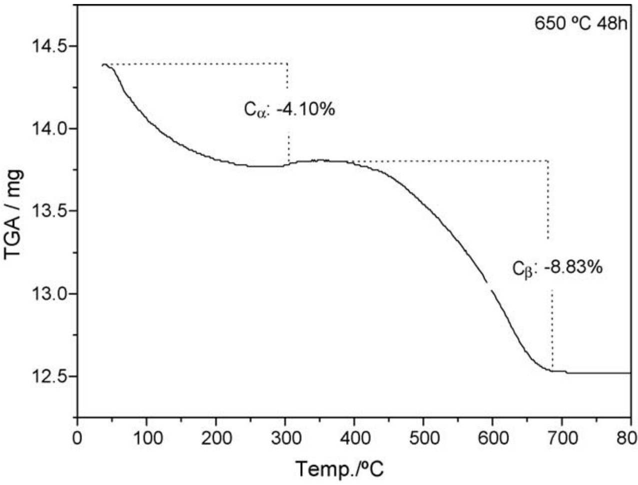

Fig. 9. TGA profile of Ni/Al_2O_3 catalyst after reaction at 650 °C for 48 h.

Fig. 10 shows the TEM images of the used catalysts taken from the stability tests. From these TEM images, no significant carbon deposits can be observed over the used plasma treated catalysts. Especially, the size of nickel particles over all catalysts did not increase after reaction, compared with the fresh catalyst, shown in Fig. 2. The plasma treated catalyst can keep very stable even at high reaction temperatures (as high as 750 °C in this work). No sintering was observed.

4. Conclusion

We have developed a novel plasma treatment and calcination method to prepare Ni/Al_2O_3 catalyst for carbon dioxide reforming of methane. The catalyst prepared this way shows an improved low-temperature activity and an enhanced stability. Compared to the reported work, methane conversion over the plasma treated catalyst has a ca. 20% increase at the same reaction temperature. The plasma treated catalyst possesses a better anti-carbon deposit performance for carbon dioxide reforming of methane, especially in relatively low temperature (650 and 750 °C), compared to the reported work. Obviously, the plasma treatment followed by calcination thermally induces a generation of specific nickel particles on the support. These particles are highly dispersed and can remain stable during reforming reactions. In addition, these highly dispersed metal species would induce better low-temperature activity. Further investigation is being carried out to clarify the mechanism how the plasma interacts with the support and metal cluster.

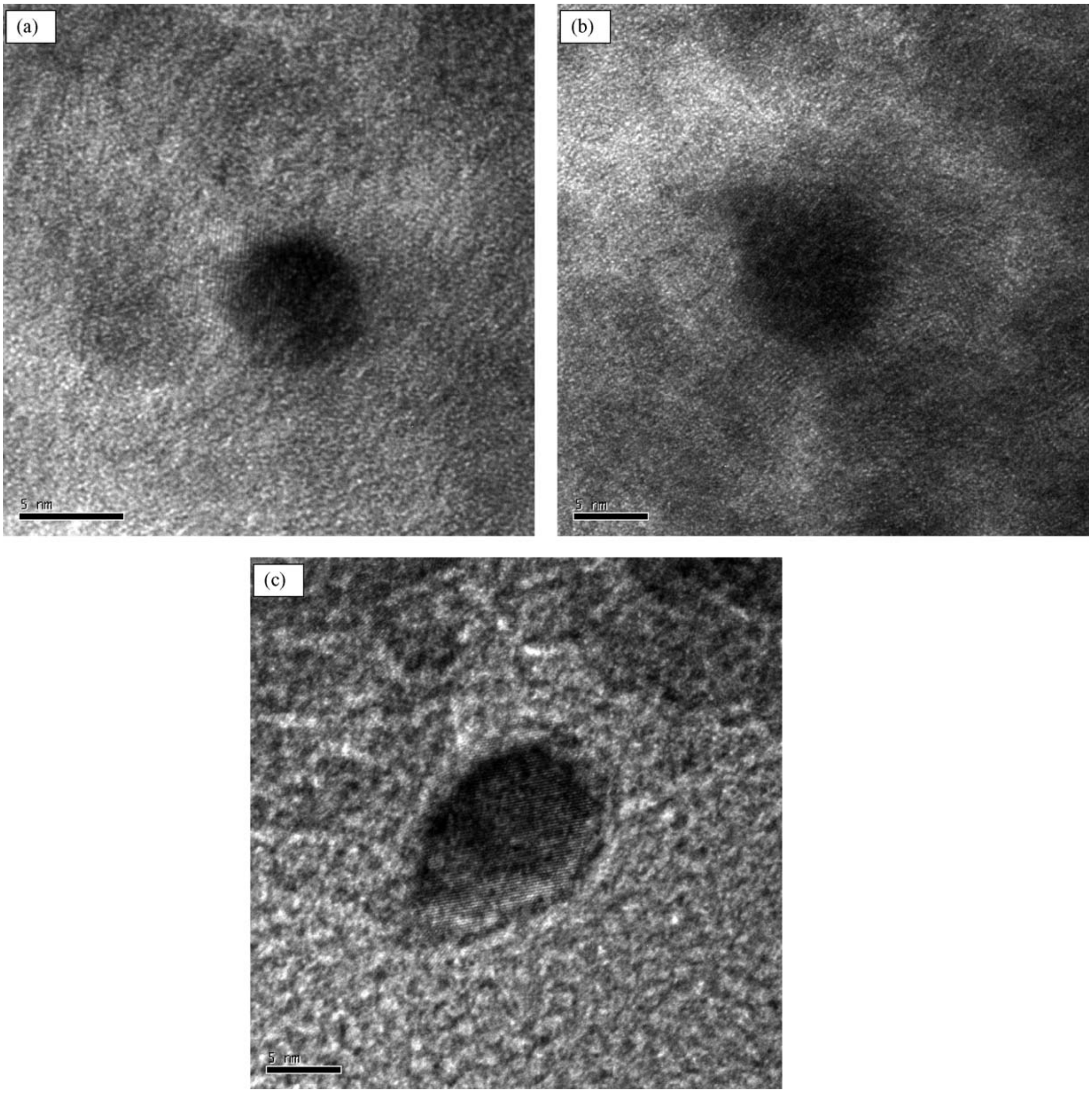

Fig. 10. TEM images of used Ni/Al_2O_3 catalysts: (a) after reaction at 550 °C for 10 h; (b) after reaction at 650 °C for 48 h; (c) after reaction at 750 °C for 48 h.

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