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Effects of ceria in CO_2 reforming of methane over Ni/calcium hydroxyapatite

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Abstract–In CO_2 reforming of methane over a calcium hydroxyapatite-supported nickel catalyst, the carbon deposition occurred more severely with increase of the methane partial pressure and at temperatures below about 1,000 K. The effects of ceria that was added as a promoter to the nickel catalyst were investigated. It was observed that the ceria not only enhanced the catalyst stability but also increased the activity, and this is considered owing to the oxygen storage capacity of ceria. The TGA analysis demonstrated that the ceria promoted the removal of the deposited carbon. The optimum Ce/Ni mole ratio was ca. 0.3/2.5. The deposited carbon could easily be removed by oxygen treatment at 1,023 K and the catalytic activity could be restored.

Key words: Calcium Hydroxyapatite, Carbon Dioxide Reforming, Ceria, Nickel, Promoter

INTRODUCTION

Catalytic reforming of CH_4 with CO_2 (CDR) has gained an increasing interest since it is intimately related to the environment as a method to mitigate the greenhouse gases and to the energy resource for the production of synthesis gas [Ashcroft et al., 1991; Inui, 1999; Rostrup-Nielsen and Bak Hansen, 1993]. CDR is practiced in industry [Rostrup-Nielsen, 1984], and it has been studied over many supported metal catalysts such as Ni-based catalysts as well as noble metal catalysts. One of the major problems in CDR is deactivation by carbon deposition that occurs more severely than in steam reforming or partial oxidation of methane, especially on nickel catalysts [Chang et al., 1996; Edwards and Maitra, 1995; Rostrup-Nielsen, 1984; Tomishige et al., 2000]. One reason is that nickel has a high affinity with carbon (so as to form such as nickle carbide), thus prone to form amorphous carbon, carbon fibers and nanotubes. Another reason is that CO_2 is a weaker oxidant than H_2O and much weaker than O_2, and thus the removal of deposited carbon by CO_2 is not easy. Noble metal catalysts are reported to be more active and have higher resistance to carbon deposition, but considering the high cost and limited availability of them, it is more practical to develop Ni-based catalysts. Nickel is usually supported on various oxides, such as alumina, silica, magnesia, zirconia, titania, ceria and zeolites, but to overcome the deactivation by carbon deposition is still a challenge.

Recently, some of MgO-containing catalysts, such as NiO-MgO solid solution [Tomishige et al., 2000] and Ni/Mg-Al oxide [Shishido et al., 2001; Tsyganok et al., 2003], have been reported to have long life, and this was attributed to highly dispersed Ni metal particles and the presence of basic MgO that are effective for inhibiting carbon deposition. Since the carbon deposition requires large ensemble sites on the metal surface, highly dispersed particles that have fewer ensemble sites are effective in preventing the carbon deposition. It is also well known that acidic supports, such as alumina, facilitates the carbon deposition. The presence of MgO will reduce the acidity of the acidic supports, and in addition, will reduce the number of large ensemble sites by forming a solid solution with NiO or sitting on the metal surface. Besides MgO, there appear several reports that show that ceria is effective for elimination of deposited carbon during partial oxidation, steam reforming or CO_2 reforming of methane [Asami et al., 2003; Dong et al., 2002; Kim et al., 2006; Mattos et al., 2002; Stagg-Williams et al., 2000]. Ceria is also reported to be effective in enhancing the activity [Cracium et al., 2002; Dong et al., 2002; Kim et al., 2006; Kusakabe et al., 2004; Mattos et al., 2002; Sharma et al., 2000; Wang and Lu, 1998]. These effects of ceria are believed to originate from its basicity and oxygen storage capacity, which effectively inhibits carbon deposition or removes deposited carbon by oxidation.

In this work a novel type of Ni-based catalyst having no oxide support, Ni/calcium hydroxyapatite ($Ca_{10}(OH)_2(PO_4)_6$) which has recently been reported to be highly active for the partial oxidation of methane [Jun et al., 2004a, b], was tested for the CO_2 reforming of methane. This work was focused on the deactivation and improvement of this catalyst. Effects of feed composition and temperature on the deactivation by carbon deposition were investigated. To improve the catalyst performance, ceria was added as the promoter and its effects on the activity and carbon deposition were investigated.

EXPERIMENTAL

The ceria-promoted catalysts were prepared by following the same procedure as described in a previous work [Jun et al., 2004b]. The pH of each of the aqueous solutions of calcium nitrate, nickel nitrate and dibasic ammonium phosphate was adjusted to 10-11 by adding ammonia water, and predetermined amounts of the solutions were mixed at room temperature with vigorous stirring for 1 h. The water was evaporated to get a thick paste and a cerium nitrate solution was added. Then the mixture was dried at 383 K overnight and finally heat treated in air at 1,073 K for 2 h to obtain the catalyst. The solid catalyst was crushed and sieved, and the particles of 40- to 80-mesh size were used for the test. The mole ratio of Ca/PO_4 employed was fixed at 10/6, which corresponds to that in calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), and Ni/PO_4 mole ratio was also

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fixed at 2.5/6, which was reported to be in the optimum range in the previous work [Jun et al., 2004a]. The mole ratio of Ce/Ni was varied up to 0.5/2.5. The ceria-promoted catalyst was designated to be $Ce_aNi_{2.5}Ca_{10}$, where a denotes (Ce/Ni)×2.5, and the un-promoted catalyst was designated to be $Ni_{2.5}Ca_{10}$.

The catalyst performance was tested by a conventional method using an 8 mm i.d. quartz-tube flow reactor as described in the previous work [Jun et al., 2004b]. The reaction temperature was measured by a thermocouple inserted from the top of the reactor and contacting directly the catalyst particles. The following experimental conditions were employed, unless specified otherwise. The total gas feed rate was 100 cm^3 (STP)/min and the CH_4 feed composition varied from 10% to 40% with the CO_2/CH_4 mole ratio of 1. Argon was used as the diluent gas. The amount of catalyst loading was 0.2 g when no diluent inert powder was used. When a smaller amount of the catalyst (0.05 g) was used in order to increase the space velocity, inert quartz powder of the same size was added and the amount of the powder mixture was 0.2 g. Here the volumetric hourly space velocity (VHSV) was defined as the total volumetric gas flow rate under STP divided by the catalyst charge. The catalyst was activated by a reactant-gas mixture containing 10% CH_4, 10% CO_2 and 80% Ar at 1,023 K for 30 min, since this was found to be effective for the catalyst activation without H_2 pretreatment. The effluent gas was analysed by a gas chromatograph with a Carboxen column (Supelco) using Ar carrier. The catalyst samples were characterized by XRD, SEM and TGA.

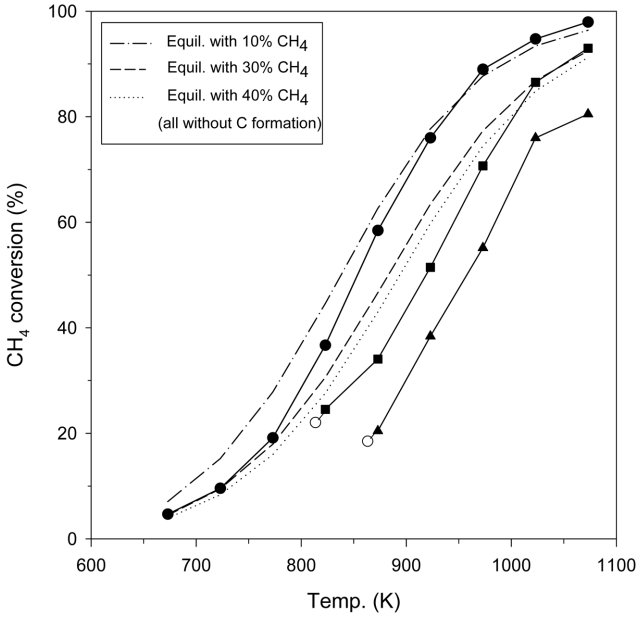

Fig. 1. CH_4 conversion over $Ni_{2.5}Ca_{10}$ in CDR with varying feed composition (CH_4 10%: ●, CH_4 30%: ■, CH_4 40%: ▲, CH_4/CO_2=1, total flow rate=100 cm^3 (STP)/min, catalyst charge=0.2 g, VHSV=30,000 $cm^3/g{\cdot}h$; '-o': the instance at which the experiment was stopped due to the reactor blocking).

RESULTS AND DISCUSSION

1. Catalyst Activation

One of the salient features of $Ni_{2.5}Ca_{10}$ in partial oxidation of methane is that this catalyst can be activated by the reacting gases only (methane+oxygen) at around 900 K [Jun et al., 2004b]. Therefore, it was tested that this catalyst could also be activated by the reacting gases only in CDR. When the activation of $Ni_{2.5}Ca_{10}$ was attempted at 1,023 K by feeding a 50% CH_4-50% CO_2 gas, it failed with significant pressure build-up due to severe carbon deposition and no CO_2 reforming occurred. The activation by a 40% CH_4-40% CO_2 gas was not successful either. But when a 10% CH_4-10% CO_2 gas was fed, the catalyst was successfully activated within 30 min at 1,023 K and the obtained CH_4 and CO_2 conversions were higher than 90%. The activation could be done successfully with a 30% CH_4-30% CO_2 at 1,023 K, but this is considered less safe because more carbon deposition would occur with higher CH_4 partial pressure.

When the activation was attempted with a 10% CH_4-10% CO_2 gas by sequentially increasing the temperature from 723 K by 50-degree intervals, the activation could be started at 823 K, where the CH_4 conversion was 48%. After 1-h operation, the temperature was increased to 873 K. After 30 min at this temperature the CH_4 conversion was 64%, but the pressure in the reactor continued to increase and after 1 h the CH_4 conversion decreased to 55%. When the temperature was subsequently increased to 923 K, the pressure increased greatly and the reactant flow was interrupted; thus the reaction could not be continued. Therefore, for each of the following sets of reaction experiments, the activation of the fresh catalyst was done at 1,023 K with the 10% CH_4-10% CO_2 gas and then the reaction temperature and/or the feed composition was adjusted to the desired value and the experiments were carried out without further activation unless specified otherwise.

2. Effects of Feed Composition and Temperature

Fig. 1 shows the CH_4 conversions over $Ni_{2.5}Ca_{10}$ with respect to different feed composition. For each feed composition, the first experiment was done at 1,073 K after the activation as described above and then the temperature was decreased by 50-degree intervals without further activation between the temperature adjustments. With the 10% CH_4 feed gas, the conversions close to the equilibrium could be obtained and the catalyst was kept active down to 673 K. When the CH_4 feed composition was 30%, the conversion decreased considerably as shown in the figure, significantly lower than the equilibrium value except above 1,023 K. When the CH_4 feed composition was increased to 40%, the conversion decreased more, lower than the equilibrium to a greater extent. Furthermore, the reaction could not be continued at 773 and 823 K for the above two cases, respectively, due to the flow interruption caused by rapid pressure build-up in the reactor.

Fig. 2 shows prolonged tests over $Ni_{2.5}Ca_{10}$ with the 10% CH_4-10% CO_2 feed gas at different temperatures. For each temperature, the fresh catalyst was loaded and activated as described above. At a reaction temperature of 1,023 K, the activity remained almost constant for 24 h and a pressure build-up was not observed. However, at a lower temperatures (823-973 K), the pressure in the reactor increased continuously and the reaction could not be continued after 3.5-5 h due to the flow interruption. The pressure build-up (or carbon deposition) was observed to be the fastest at 923 K.

As seen above, the coke formation was sensitive to the reactant composition and temperature. This is consistent with the prediction

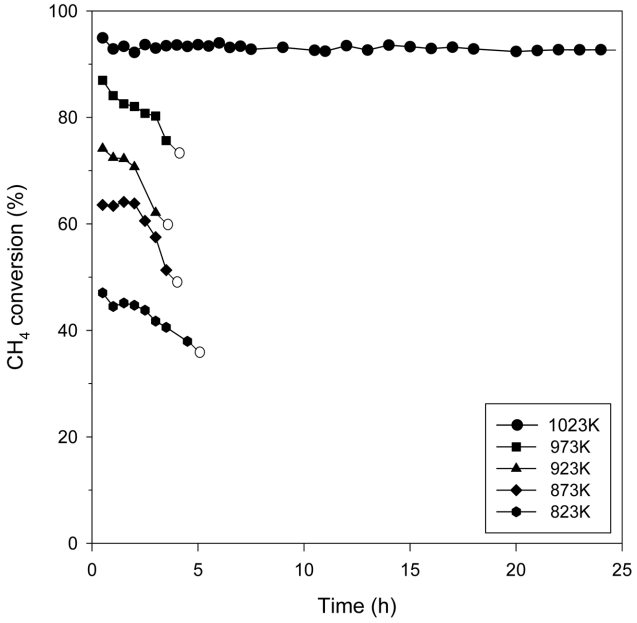

Fig. 2. Deactivation of $Ni_{2.5}Ca_{10}$ not diluted with quartz powder at different temperatures with 10% CH_4 feed in CDR (CH_4/CO_2=1, VHSV=30,000 $cm^3/g \cdot h$; '-o': reactor blocking).

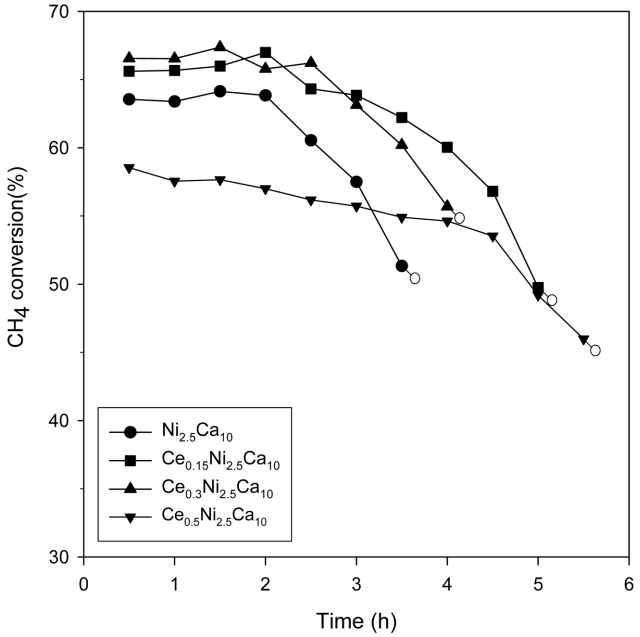

Fig. 3. Deactivation test for the catalysts not diluted with quartz powder with 10% CH_4 feed at 873 K (CH_4/CO_2=1, VHSV= 30,000 $cm^3/g \cdot h$; '-o': reactor blocking).

by the thermodynamic analysis [Edwards and Maitra, 1995; Fraenkel et al., 1986], which shows that carbon deposition is less favorable with lower CH_4 pressures and at higher temperature. The less favorable carbon deposition at the higher temperatures may be explained by the fact that the deposited carbon could be removed favorably by the reaction with CO_2 ($C+CO_2 \rightarrow 2\,CO$: $\Delta H^o=+172.5$ kJ). It has also been reported from experiments that the carbon deposition occurs rapidly at around 973 K over Ni [Asami et al., 2003; Wang and Lu, 1999], which is similar to our result. It may be proposed that at the first stage the activation of the nickel catalyst is achieved (at 823 K and above) by reduction of NiO with CH_4, which produces metallic nickel, CO and H_2, and then the produced CO and H_2 can accelerate the reduction of NiO. However, carbon deposition on the metallic nickel is soon followed by decomposition of CH_4, which is the main cause of the catalyst deactivation by covering the metal surface [Dong et al., 2002]. The carbon deposition occurs severely under thermodynamically favorable conditions as mentioned above.

3. Effects of Ceria Promoter

Performance of the ceria-promoted catalysts was compared with the un-promoted catalyst at 873 K. This low temperature was chosen for the rapid assessment of the deactivation. Fig. 3 shows the results obtained for the catalysts not diluted with quartz powder. Over the promoted catalysts the reaction could last longer. From about 2 h on-stream increase of the reactor pressure was observed and the deactivation appeared to be accelerated due to the pressure build-up. The initial conversions obtained over $Ce_{03}Ni_{2.5}Ca_{10}$ (CeO_2 content=4.2 wt%) and $Ce_{0.15}Ni_{2.5}Ca_{10}$ (CeO_2 content=2.2 wt%) were higher than the conversion over the un-promoted catalyst and very close to the equilibrium; the H_2/CO ratio was near 0.9. The initial activity of $Ce_{0.5}Ni_{2.5}Ca_{10}$ (CeO_2 content=6.7 wt%) was the lowest, and this is considered due to physical blocking of a great part of active nickel surface by too much CeO_2. However, the reaction experiment could be done for the longest time before the reactor blocking. The catalysts after the reactor blocking were collected and weighed, and the amount of deposited carbon in each catalyst was similar to one another, that is ca. 1±0.1 g carbon/g-cat.

When the reactor was charged with the catalyst only, almost complete blocking of the catalyst bed occurred in a relatively short time (<6 h) below 1,023 K. Therefore, the catalyst was mixed with quartz powder and then the test was carried out under higher VHSV at 873 K. In this case, as shown in Fig. 4, practically no pressure build-up was observed for 12 h. This indicates that the inert powder pre-

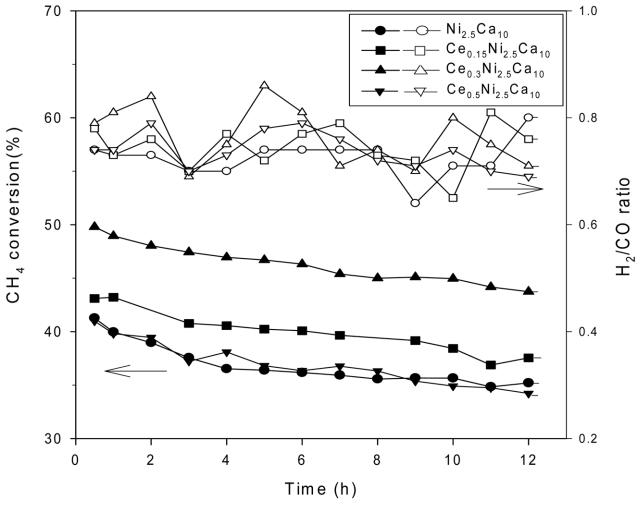

Fig. 4. Deactivation test in CDR with 10% CH_4 feed at 873 K for the catalysts diluted with quartz powder (closed symbols: CH_4 conversion, open symbols: H_2/CO ratio; CH_4/CO_2=1, catalyst charge=0.05 g, quartz powder charge=0.15 g, VHSV =120,000 $cm^3/g \cdot h$).

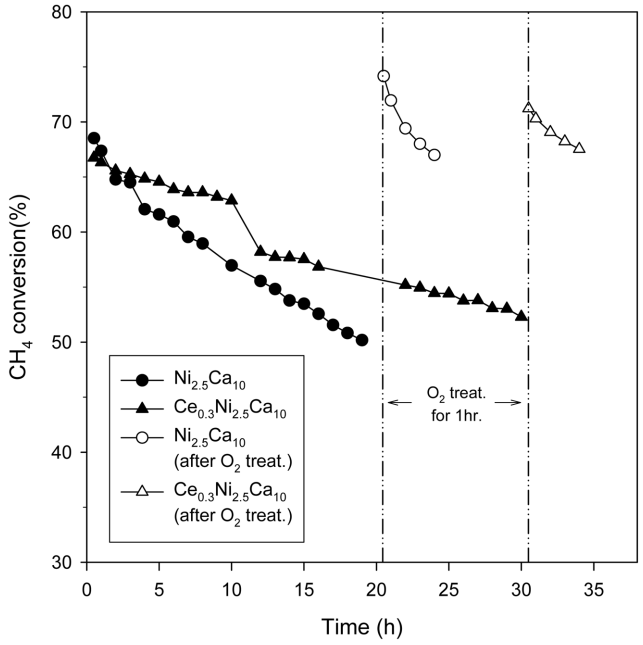

Fig. 5. Catalyst durability test with 30% CH_4 feed at 1,023 K (catalyst charge=0.05 g, quartz powder charge=0.15 g, VHSV= 120,000 $cm^3/g \cdot h$).

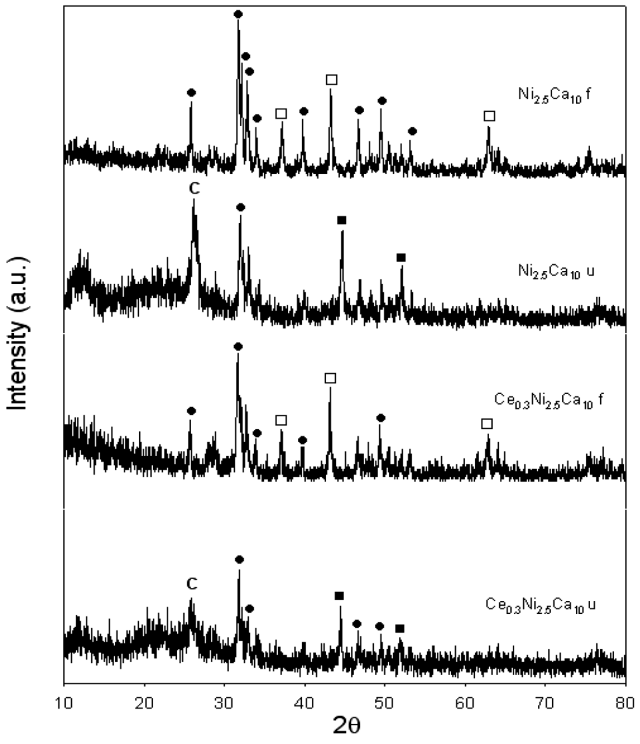

Fig. 6. X-ray diffractograms for $Ni_{2.5}Ca_{10}$ and $Ce_{0.3}Ni_{2.5}Ca_{10}$ before(f) and after(u) CO_2 reforming at 873 K (●: $Ca_{10}(PO_4)_6(OH)_2$; □: NiO; ■: Ni; C: carbon).

vents complete blocking of the catalyst bed by providing channels for the gas to flow even though carbon deposition occurs to a considerable extent. The activity decreased gradually but accelerated deactivation was not observed. Similar to the results in Fig. 3, $Ce_{03}Ni_{2.5}Ca_{10}$ showed the highest activity. The decrease of the CH_4 conversion in the absolute value for 12 h was nearly the same (5-6%) for the four catalysts, but the relative decrease was the smallest for $Ce_{03}Ni_{2.5}Ca_{10}$. The H_2/CO ratios were nearly the same for the four catalysts (mostly between 0.7 and 0.8). Although there was some scattering, the H_2/CO ratio changed little with time.

Another catalyst durability test was carried out at 1,023 K with a 30% CH_4 feed and the results are shown in Fig. 5. Since the CH_4 feed concentration was higher, the deactivation occurred much more rapidly when compared with the result shown in Fig. 2 with a 10% CH_4 feed. Nonetheless, the ceria-promoted catalyst exhibited more stable behavior than the un-promoted one. When the deactivated catalysts were treated with 10% oxygen in Ar for 1 h in order to remove the deposited carbon, the activity was fully restored. The fact that the restored activity was higher than the initial activity may be explained as follows. Since the activation of the fresh catalyst was done with the reactant gases, carbon deposition may have occurred to some extent during the activation. On the contrary during the regeneration by oxygen, the deposited carbon could almost completely be removed and hence the activity right after the regeneration can be higher. Anyway, this experiment suggests that the catalyst can be relatively easily regenerated. Although the catalyst in this work seemed to be less resistant to the coke formation compared with other nickel catalysts reported in the literature, this catalyst could be stably operated for a long period under certain conditions, especially at 1,023 K with 10% CH_4 feed, as shown in Fig. 2.

The XRD patterns of fresh and used catalysts are shown in Fig. 6. Here the used catalysts are the samples presented in Fig. 3 after the reaction at 873 K. Whether the ceria was present or not, the peaks for calcium hydroxyapatite seemed to change little before and after the reaction. Almost all the NiO in the fresh sample was reduced to metallic Ni after the reaction. On the used samples, however, considerable amounts of deposited carbon (the peak at around 27° of 2θ) were observed. The amount of carbon on the un-promoted catalyst appeared larger than that on the promoted catalyst. It was also observed by SEM that large amounts of carbon nanofibers or nanotubes whose diameter ranged from 60 to 130 nm were present on the used samples, and beside these some amorphous carbon was also observed (Fig. 7).

The TGA results (Fig. 8) clearly show that as the ceria content increased removal of the deposited carbon became easier: that is, the peak maximum temperature and the temperatures at which the removal started and practically ended were all decreased. The temperature at which the removal practically ended was lower by about 70 K for $Ce_{0.3}Ni_{2.5}Ca_{10}$ and $Ce_{0.5}Ni_{2.5}Ca_{10}$ than that for the un-promoted catalyst (Note: The area under the peak is proportional to the amount of deposited carbon in the analyzed sample. However, the area in Fig. 8 does not represent the average amount of the carbon in the entire used catalyst because the amount of sample taken for TGA is small (a few milligrams) and the distribution of the carbon may not be uniform throughout the entire used catalyst. Therefore, the peak area is not important in this case but the position gives us more meaningful information.).

Although carbon deposition is thermodynamically significant under the reaction conditions, it has been suggested that carbon deposition would be prevented if the reaction were controlled kinetically by using a suitable catalyst [Edwards and Maitra, 1995]. It has been

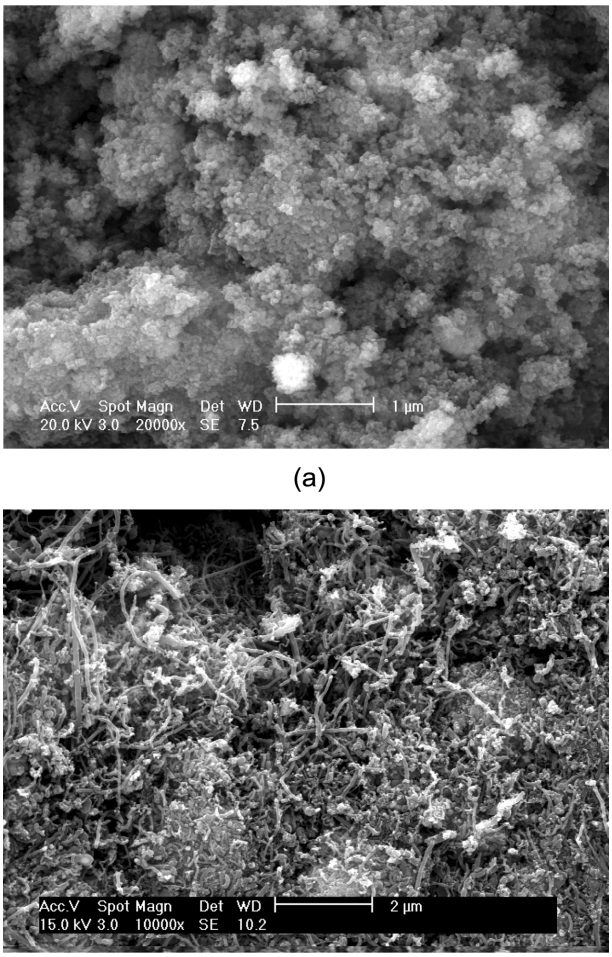

Fig. 7. SEM images of $Ce_{0.3}Ni_{2.5}Ca_{10}$ (a) before and (b) after CDR at 873 K.

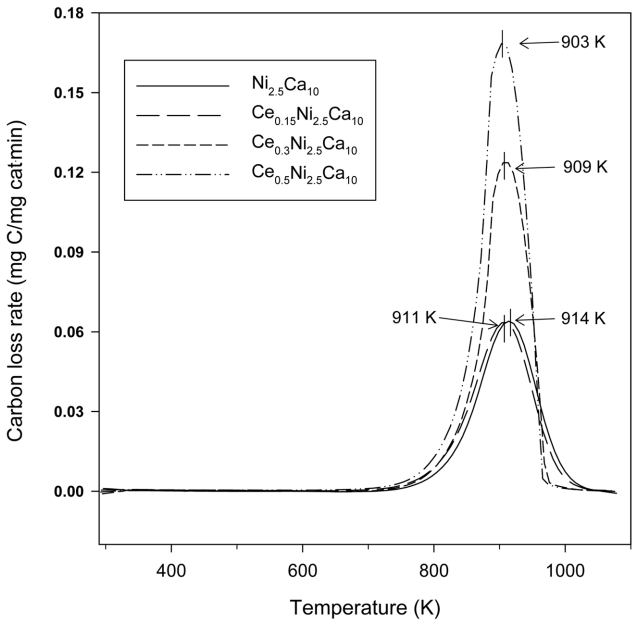

Fig. 8. TGA results under flowing air for the samples after CDR at 873 K.

reported that ceria as the support or the promoter enhances the activity and stability of Ni in CO_2 reforming of methane. The improvement of the catalytic performance was attributed to the lattice oxygen in ceria that participates in the removal of carbon deposit by oxidation to CO, which in turn leaves the active metal surface more clean [Dong et al., 2002], or a strong metal-support interaction which results in increase of reducibility of nickel and increase of the number of the active sites [Asami et al., 2003; Wang and Lu, 1998]. These suggestions may also be applicable to our system, although the latter was not directly confirmed in this work. The consumed lattice oxygen in ceria can be replenished by CO_2 [Sharma et al., 2000]. The results in this work clearly showed that the oxidative property of ceria was effective for the removal of deposited carbon as well as the reforming of methane and thus increased the catalyst stability and activity.

CONCLUSIONS

In CO_2 reforming of methane over a nickel catalyst, ceria added as a promoter was found to be effective for the removal of deposited carbon. This is considered due to the oxidative property of lattice oxygen in ceria. Consequently, the ceria promoter enhanced the catalyst stability as well as the activity. The optimum Ce/Ni ratio was determined to be 0.3/2.5. When the ceria content was too high, the activity decreased due to physical blocking of the active surface.

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