Highly stable Ni catalyst supported on Ce–ZrO_2 for oxy-steam reforming of methane

Hyun-Seog Roh[a], Ki-Won Jun[a], Wen-Sheng Dong[a], Sang-Eon Park[a,*] and Young-Soon Baek[b]

[a] Catalysis Center for Molecular Engineering, Korea Research Institute of Chemical Technology, PO Box 107, Yusong, Taejon 305-600, Korea
[b] LNG Technology Research Center, Korea Gas Corporation, 973 Dongchun-Dong, Yeonsu-Ku, Incheon 406-130, Korea

Received 30 November 2000; accepted 4 April 2001

A novel catalyst, Ni/Ce–ZrO_2, exhibits very high catalytic activity and stability even in the stoichiometric steam reforming of methane ($H_2O/CH_4 = 1$). Furthermore, when it was employed in oxy-steam reforming, it gave enhanced CH_4 conversion (99.1%) at 750 °C and the activity was maintained for 100 h. The high catalyst stability is mainly ascribed to the synergistic effect of the Ce modifier resulting from high capacity to store oxygen and high ability to produce mobile oxygen.

KEY WORDS: Ni/Ce–ZrO_2; methane; steam reforming; oxy-steam reforming; Ce modifier

1. Introduction

Production of hydrogen has received much attention in recent years, due to the importance of hydrogen as a clean source of energy as well as the increased demand in chemical industry [1–3]. Steam reforming of methane (SRM) is a widely practiced technology for hydrogen production. The reaction is highly endothermic. Although stoichiometry for the SRM suggests that only one mole of water is required for one mole of methane ($CH_4 + H_2O \rightarrow CO + 3H_2$), usually excess steam is used to reduce carbon formation. Because of the excess steam, the cost of operating an SRM plant increases. Furthermore, the H_2/CO ratio is over 3 in SRM, which does not fit for methanol synthesis or Fischer–Tropsch synthesis. As an alternative, partial oxidation of methane (POM) has advantages such as mild exothermicity, high conversion, high selectivity, suitable H_2/CO ratio and very short residence time [3]. However, POM has also disadvantages such as explosion danger and carbon formation. Due to these demerits, catalytic POM has not been commercialized even though it is estimated to be more economical than SRM [1]. As another alternative, oxy-steam reforming (combination of POM and SRM) could be considered. By co-feeding steam and oxygen, one can avoid explosion danger in POM and lessen additional steam cost in SRM, and the H_2/CO ratio can be controlled by changing the feeding rate of steam or oxygen per methane. Furthermore, one can expect enhanced CH_4 conversion and H_2 yield by combination of these two reforming reactions. Besides these advantages, increasing the portion of exothermic POM reaction could reduce required energy for the reforming reaction. In 1991, Green and co-workers [4] reported that 1% Ir/Al_2O_3 showed high activities with different compositions of CH_4, O_2, and CO_2. In 1994, Choudhary *et al.* [5] reported syngas formation by coupled exothermic oxidative conversion and endothermic CO_2 and steam reforming of methane over NiO/CaO catalyst. They suggested that the coupled process can be made mildly exothermic, nearly thermoneutral, or mildly endothermic by manipulating the process conditions.

Recently, zirconia as a support was applied to Ni catalysts for CO_2 reforming of methane and good results were reported [6,7]. Furthermore, Ni/Ce–ZrO_2 showed high activity and stability in partial oxidation of methane without catalyst deactivation [8]. Based on the previous results, in the present work, Ce–ZrO_2-supported Ni catalyst was applied to SRM using a stoichiometric feed mixture ($H_2O/CH_4 = 1.0$) and oxy-steam reforming of methane (OSRM). As a result, it has been found that Ni supported on Ce-doped ZrO_2 is very active and stable in SRM even under severe conditions and exhibits high activity as well as stability in OSRM.

2. Experimental

Support materials employed in this study were monoclinic ZrO_2 (99%, Strem Chemicals), $MgAl_2O_4$ (99%, Johnson Matthey), MgO (99%, Aldrich Chemicals), CeO_2 (99%, Aldrich Chemicals), and Ce-doped ZrO_2. Ce-doped zirconia support was prepared by the sol–gel method using a mixture of zirconyl chloride and the corresponding salt of Ce [7,8]. The weight ratio of ZrO_2 to CeO_2 was 4 : 1. The modified zirconia support was calcined at 800 °C for 6 h in air. Supported Ni (15 wt%) catalysts were prepared by the molten-salt method using its nitrate source [8,9]. The catalyst samples were calcined at 550 °C for 6 h in air. Catalytic activity measurements were conducted in a fixed-bed quartz reactor with inner diameter of 4 mm at atmospheric pressure. The reactant gas stream consisted of CH_4 and H_2O with a molar ratio of 1 : 1 both in SRM and OSRM. The ra-

---

[*] To whom correspondence should be addressed.

tio of O_2/CH_4 in the feed gas was changed from 0.5 to 0 in OSRM. In all the reactions, CH_4 feed flow rate was fixed to 30 cm^2/min. Prior to each catalytic measurement, the catalyst was reduced in H_2/N_2 (5 vol% H_2) at 700 °C for 2 h. Effluent gases from the reactor were analyzed by means of a gas chromatograph (Chrompack CP9001) equipped with a thermal conductivity detector (TCD). The GC column used in this study was a fused silica capillary column (CarboPLOT P7). The BET specific surface areas were measured by nitrogen adsorption at 77 K using a Micromeritics instrument (ASAP-2400). X-ray diffraction (XRD) patterns were recorded using a Rigaku 2155D6 diffractometer (Ni-filtered Cu Kα, 40 kV, 50 mA). Temperature-programmed reduction (TPR) was carried out in a conventional apparatus [10] using 5% H_2/N_2 gas with a heating rate of 10 °C/min. X-ray photoelectron spectroscopy (XPS) measurements were performed at room temperature on a VG ESCALAB 210 spectrometer, with Al Kα radiation generated at 300 W. The analyses were operated at a pass energy of 20 eV and a step size of 0.1 eV. Pulse reactions were carried out to estimate the amount of mobile oxygen in the supports according to the method described by Hayakawa *et al.* [11]. 200 mg of each support was loaded in a conventional quartz reactor. Before pulse reaction the sample was pretreated in He at 800 °C for 2 h. Then hydrogen pulse (1 ml × 7) reaction was started at 800 °C using pure H_2 to react with the mobile oxygen species, leading to reduction of the support, and then CO_2 was pulsed over the support, resulting in re-oxidation of the reduced support with converting CO_2 into CO.

3. Results and discussion

In commercial SRM processes, Al_2O_3 and $MgAl_2O_4$ have been used as supports due to their thermal stabilities at high temperature. Especially the latter is preferred, because it is less acidic than alumina resulting in lower coke deposition and it has significant surface area due to its spinel structure. Monoclinic zirconia also has thermal stability at high temperature as well as a considerable surface area. Furthermore, because it has both basic and weak acidic sites, zirconia could be resistant to coke formation [6]. In addition to these superior physical properties, the surface area of zirconia can be increased by the change of its phase from monoclinic to tetragonal using doping of other metals. The modification of a zirconia support with ceria reveals the most profound effect for coke resistance of the catalyst [7]. In previous results, Ni/Ce–ZrO_2 showed high activity at high GHSV as well as high stability in POM [8].

Table 1 summarizes the BET specific surface areas and Ni surface areas of the catalysts employed in this study. The BET surface area of Ce–ZrO_2 used in this study is 55 m^2/g, whereas that of undoped zirconia is 18 m^2/g. This high surface area of Ce–ZrO_2 is due to the Ce-doping effect which makes zirconia a stable tetragonal phase, which was confirmed by XRD analysis. It seems that the BET surface area of each catalyst depends on that of the support because the Ni surface area is much smaller than the total surface area. Moreover, it is hard to correlate the total surface area with the Ni surface area, which would be predominantly affected by support-dependent Ni dispersion.

Table 1
Surface areas of the supported Ni catalysts.

Surface area (m^2/g)	Catalyst				
	Ni/ Ce–ZrO_2	Ni/ ZrO_2	Ni/ CeO_2	Ni/ MgO	Ni/ $MgAl_2O_4$
BET[a]	40	13	3	16	18
Ni[b]	0.76	1.04	–	0.71	1.96

[a] Estimated from N_2 adsorption at −196 °C.
[b] Estimated from H_2 adsorption at 50 °C.

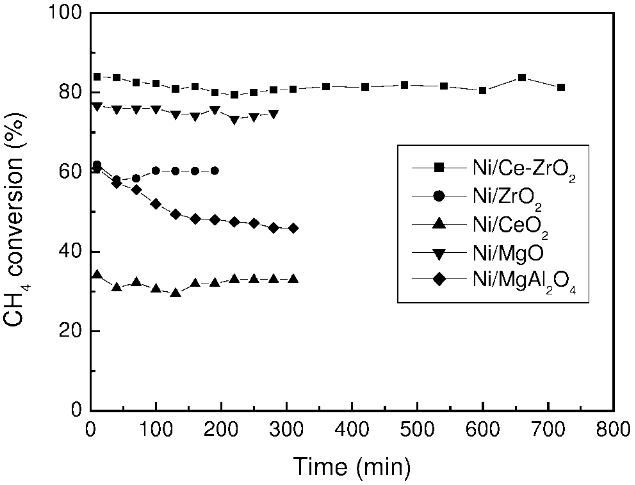

Figure 1. Change in CH_4 conversion with time on stream in stoichiometric steam reforming reaction. Conditions: CH_4 30 cm^2/min, H_2O/CH_4 = 1.0, catalyst amount 50 mg, temperature 750 °C.

Table 2
Reaction activities over supported Ni catalysts in SRM.

Catalyst	H_2 yield (%)	CO yield (%)	H_2/CO	H_2/CO_x
Ni/Ce–ZrO_2	87.0	78.2	3.4	3.2
Ni/ZrO_2	61.8	51.4	3.8	3.2
Ni/CeO_2	36.7	21.8	5.1	3.3
Ni/MgO	72.5	52.9	3.3	3.0
Ni/$MgAl_2O_4$[a]	47.8	32.1	4.4	3.2

[a] Data obtained after 6 h in SRM.

First of all, the catalysts were examined for SRM using stoichiometric feed (steam/carbon = 1.0). In order to illustrate stability in stoichiometric SRM, the change in CH_4 conversion is shown in figure 1 with time on stream over supported Ni catalysts. As can be clearly seen, Ni/$MgAl_2O_4$ remarkably deactivated with time on stream, which is most likely due to the carbon formation, but the other catalysts kept their activities. Especially, Ni/Ce–ZrO_2 executed SRM under low steam per carbon ratio (S/C = 1.0) without deactivation for 12 h. Table 2 presents H_2 yields, CO yields, H_2/CO ratios, and H_2/CO_x ratios estimated on the supported Ni catalysts in SRM. Ni/Ce–ZrO_2 showed the highest H_2

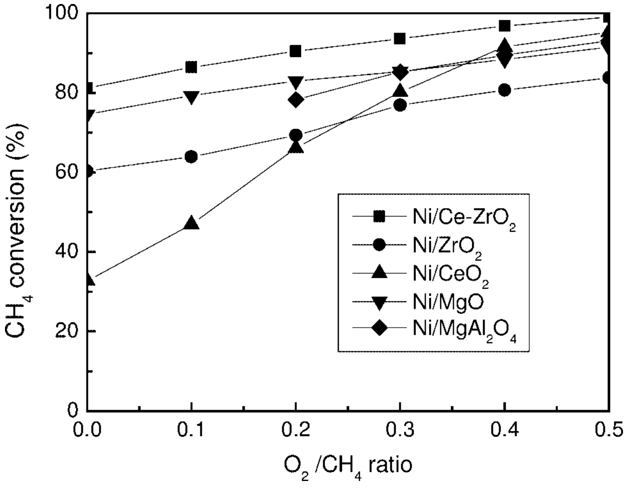

Figure 2. Dependence of CH_4 conversion on O_2/CH_4 ratio in oxy-steam reforming reaction. Conditions: CH_4 30 cm^3/min, $H_2O/CH_4 = 1.0$, catalyst amount 50 mg, temperature 750 °C.

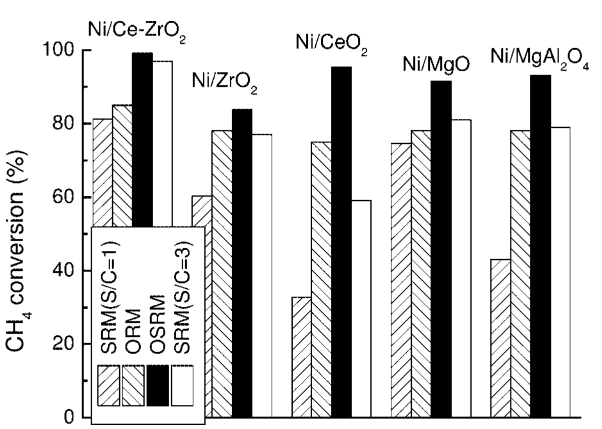

Figure 3. Dependence of CH_4 conversion on the reaction types over supported Ni catalysts.

yield and CO yield among the catalysts examined in this work. The trends of both H_2 and CO yield are similar to that of CH_4 conversion. Generally, the catalyst with high activity shows rather low H_2/CO ratio. It is due to the fact that the water–gas shift (WGS) reaction is more negligible when the amount of excess steam is relatively small. Thus, Ni/CeO_2, which showed the lowest activity, showed the highest H_2/CO ratio. H_2/CO_x ratios on the catalysts are in the range of 3.0–3.3 thus showing little difference.

The various supported Ni catalysts mentioned above were also examined with change of O_2/CH_4 ratio at 750 °C, and their activities in terms of CH_4 conversion are presented in figure 2. In this figure, the data are given only for the catalysts that show stable activities for at least 6 h under the identical reaction conditions. Ni/$MgAl_2O_4$ showed 93.1% CH_4 conversion at the O_2/CH_4 ratio of 0.5. As the O_2/CH_4 ratio decreased, CH_4 conversion also decreased, and 78.3% CH_4 conversion was obtained at the O_2/CH_4 ratio of 0.3. However, this catalyst deactivated with time on stream below the O_2/CH_4 ratio of 0.2; consequently continuous experiments could not be done due to carbon formation. This result indicates that Ni/$MgAl_2O_4$ is rather susceptible to carbon formation compared with the other catalysts. Yamazaki *et al.* [12] reported a similar result that under the condition of low steam/carbon ratio ($H_2O/CH_4 = 1.0$) a commercial reforming catalyst (Ni/Al_2O_3–MgO) deactivated due to carbon formation, but 3 mol% Ni/MgO showed stable CH_4 conversion of 90% at 850 °C and 20 000 h^{-1}. Generally, the CH_4 conversion is proportional to the O_2/CH_4 ratio. As the O_2/CH_4 ratio increases, CH_4 conversion increases. In the case of Ni/MgO, CH_4 conversion increased from 74.6 to 91.5% with the increase in O_2/CH_4 ratio from 0 to 0.5. In the case of Ni/CeO_2, though CH_4 conversion was relatively low (32.8%) at zero O_2/CH_4, it increased drastically with increasing O_2/CH_4 ratio, and finally it reached 95.3%, which is higher than that of Ni/MgO, at the O_2/CH_4 ratio of 0.5. This seems to be due to the high oxygen capacity of ceria, which would probably result in effective oxygen transfer during oxy-steam reforming. In other words, the ability to produce mobile oxygen species from oxygen molecules is higher than that from water molecules. Ni/ZrO_2 showed stable activity in the range of 60.3–83.8% depending on O_2/CH_4 ratio. The Ce modification in the support resulted in much more enhanced catalytic performance – the resultant Ni/Ce–ZrO_2 showed the highest CH_4 conversion in any range of O_2/CH_4 ratio. CH_4 conversion was 81.2% at zero O_2/CH_4 ratio, and it increased with increasing the ratio and finally it reached 99.1% at O_2/CH_4 ratio of 0.5. It can be suggested that Ni/Ce–ZrO_2 can mobile oxygen species, which play a beneficial role in producing syngas, from water molecules as well as oxygen molecules. This suggestion is supported by both TPR results and mobile oxygen data explained later. In all cases, O_2 conversions were 100%, namely no oxygen peak was detected. This indicates that POM was executed primarily and then SRM and WGS reactions were carried out.

The catalytic properties of the supported Ni catalysts have been compared parallel with different types of reforming reactions and the results are summarized in figure 3. From this figure, it is apparent that CH_4 conversion in OSRM showed the highest value among all the reactions examined. Especially, CH_4 conversions in OSRM were higher than those in SRM using the feed of $H_2O/CH_4 = 3$. For example in OSRM over Ni/Ce–ZrO_2, CH_4 conversion was 99.1% which is even higher than that (97.0%) in SRM with S/C ratio of 3. This result offers the possibility that excess steam (at least 1 mole per 1 mole methane) in the present SRM process can be replaced by oxygen (at most 0.5 mole per 1 mole methane), which would bring the benefit of decreasing additional steam cost. Furthermore, combined steam and oxy-reforming could be carried out continuously in an adiabatic reactor without supply of heat owing to the combination of exothermic POM and endothermic SRM. Besides these advantages, explosion danger in POM could be eliminated due to the steam introduction.

With the Ni/Ce–ZrO_2 catalyst, reaction data such as CH_4 conversion, CO yield, H_2/CO ratio, and H_2/CO_x ratio depending on reaction type are summarized in table 3. The CO yield is quite dependent on the reaction type. In SRM using

Table 3
Comparison of the activity over $Ni/Ce–ZrO_2$ among various reaction types.

Type	CH_4 conv. (%)	CO yield	H_2/CO ratio	H_2/CO_x ratio
OSRM[a]	99.1	67.9	3.4	2.3
POM [8]	85.0	76.3	2.1	1.9
SRM (S/C = 3.0)	97.0	67.0	4.7	3.4
SRM (S/C = 1.0)	81.2	78.0	3.3	3.2

[a] Conditions: CH_4 30 cm^3/min, O_2 15 cm^3/min, H_2O in gas 30 cm^3/min, catalyst amount 50 mg, temperature 750 °C. In all reactions, CH_4 flow rate was 30 cm^3/min for comparison.

a feed of $H_2O/CH_4 = 3$ and OSRM, owing to the water–gas shift (WGS) reaction ($CO + H_2O \rightarrow H_2 + CO_2$) resulting from using excess steam, rather low CO yield was obtained. In POM and SRM using a feed of $H_2O/CH_4 = 1$, rather high CO yield was attained though CO yield was still lower than CH_4 conversion. This can be explained as follows. In the stoichiometric SRM, the WGS reaction was still executed due to the reaction between an unconverted water molecule and a produced CO molecule. On the other hand, in POM, because the ratio of O_2/CH_4 was slightly higher than stoichiometry, somewhat CO_2 formation takes place *via* total combustion [8]. Another implication can be drawn from the data of H_2/CO ratio and H_2/CO_x ratio. The ratio of H_2/CO was 2.1 in POM and more than 3.0 in SRM due to the WGS reaction. In OSRM, H_2/CO_x was 2.3 which is adjacent to 2.0, suggesting that POM was carried out totally and a small portion of SRM and WGS reaction took place. The ratio of H_2/CO_x was 3.4 in the SRM with excess steam and 3.2 in the stoichiometric SRM, indicating that the WGS reaction becomes more considerable with higher H_2O/CH_4 ratio. From the above results, it is evident that in OSRM, $Ni/Ce–ZrO_2$ is more active and stable than $Ni/MgAl_2O_4$, which is widely used in steam reforming catalysts, and Ni/MgO, which has been reported as a fairly good POM catalyst. The outstanding catalytic properties of $Ni/Ce–ZrO_2$ can be explained as follows. The presence of ceria has beneficial influence on the catalyst performance such as increasing concentration of the highly mobile oxygen species. The role of ceria in the catalyst is assigned to form a thermally stable solid solution with zirconia and to give high capacity of oxygen storage [13]. From TPR study, it was found that the interaction with zirconia leads to the easier reduction of ceria resulting in effective oxygen transfer *via* a redox cycle [8]. The TPR patterns of Ni/ZrO_2, Ni/CeO_2 and $Ni/Ce–ZrO_2$ are shown in figure 4. While a clear reduction peak was detected at 880 °C on ceria itself [8], in the case of Ni/CeO_2, two obvious peaks were observed. One (peak maximum = 410 °C) is attributable to the reduction of NiO, and the other (peak maximum = 880 °C) is attributable to the reduction of ceria support. For Ni/ZrO_2, broad and unresolved reduction peaks with maximum at about 400 and 510 °C are observed. This suggests that there are a lot of NiO_x sites which are strongly interacted with ZrO_2 but different in the degree of this interaction. $Ni/Ce–ZrO_2$ exhibits two kinds of peaks without any obvious peak at 640 °C which was seen in the $Ce–ZrO_2$ support [8]. This is possibly due to the fact that strong interaction between Ni and $Ce–ZrO_2$ makes ceria more reducible by H_2, which probably helps to produce mobile oxygen during the reforming reaction. Besides, the reduction of NiO is retarded and the reduction range is widened, when Ni is supported on $Ce–ZrO_2$ compared with Ni/CeO_2. The first, sharp peak can be assigned to relatively free nickel oxide. The second, broad peak can be assigned to complex NiO_x species which strongly interact with the support, and it seems to be concurrent with ceria reduction.

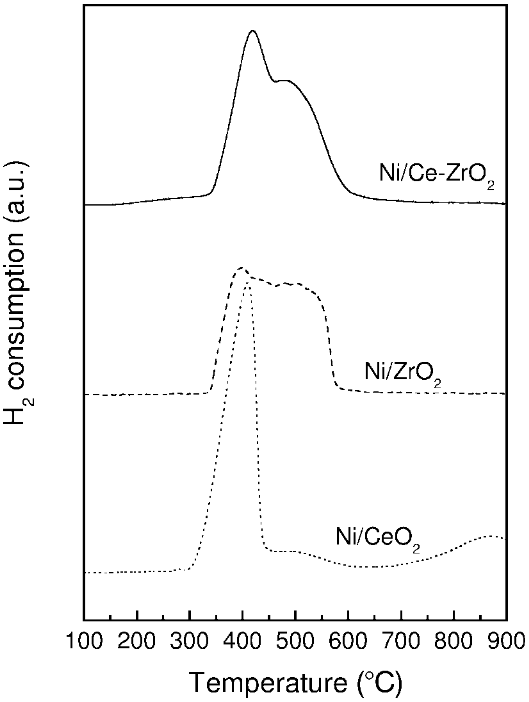

Figure 4. TPR patterns of $Ni/Ce–ZrO_2$, Ni/ZrO_2, Ni/CeO_2.

Table 4
XPS binding energies of Ni $2p_{3/2}$ and Ni surface concentration data of supported Ni catalysts.

	Catalyst				
	15% Ni/ $Ce–ZrO_2$	3% Ni/ $Ce–ZrO_2$	15% Ni/ ZrO_2	15% Ni/ CeO_2	15% Ni/ MgO
Ni BE (eV)	854.4 857.0	856.4	855.3	854.4	856.7
Ni surf. conc. (%)	15.6	3.3	16.1	30.4	18.0

The XPS binding energies (BE) of Ni $2p_{3/2}$ electrons and surface Ni concentration data in the catalysts are shown in table 4. In the case of Ni/CeO_2, the Ni $2p_{3/2}$ BE is 854.4 eV, which is characteristic of free NiO species. The BE of Ni/ZrO_2 is 0.9 eV higher than that of Ni/CeO_2, indicating the existence of interaction between NiO and ZrO_2. Ni/MgO shows much higher BE shift (+2.3 eV). It is known that Ni/MgO forms a solid solution, whereby a very strong interaction between NiO and MgO would result. In the case of $Ni/Ce–ZrO_2$, two Ni $2p_{3/2}$ BEs appear. One is 854.4 eV, which is assigned as free NiO species, and the other is 857.0 eV, which can be attributable to NiO_x species strongly

Table 5
Mobile oxygen in the supports or catalysts.

Sample	Mobile oxygen (μmol/g-sample)	Mobile oxygen[a] (%)
Ce–ZrO_2	254.7	1.660
CeO_2	251.5	2.160
ZrO_2	5.25	0.032
MgO	3.36	0.014
$MgAl_2O_4$	–	–
3% Ni/Ce–ZrO_2	228.8	1.580
15% Ni/Ce–ZrO_2	214.9	1.750

[a] Percentage in total oxygen in the support.

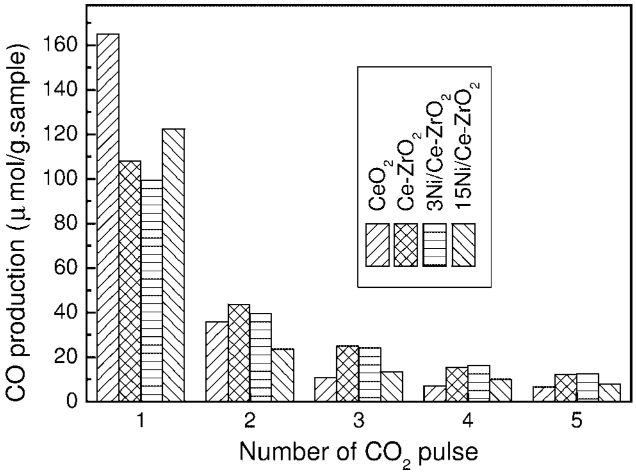

Figure 5. CO production with CO_2 pulse over supports or catalysts.

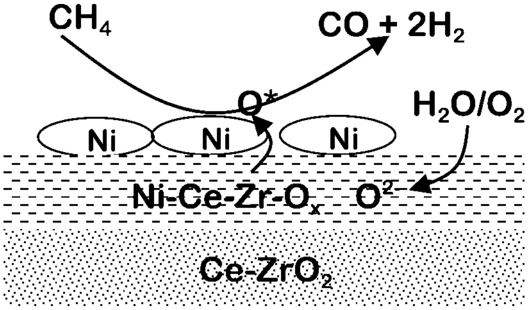

Figure 6. Schematics of producing syngas over Ni/Ce–ZrO_2 catalyst.

interacted with Ce–ZrO_2. This result is quite consistent with the TPR pattern of Ni/Ce–ZrO_2. For the 3% Ni/Ce–ZrO_2 sample, the BE of Ni is 856.4 eV. Ni surface concentrations are strongly dependent on the supports even though the bulk concentrations are the same. The Ni surface concentration of Ni/CeO_2 is 30.4% which is two times higher than the bulk concentration. This is due to the low surface area of CeO_2 and little interaction between Ni and CeO_2 which is consistent with the TPR pattern of Ni/CeO_2. Ni/MgO and Ni/ZrO_2 show 18.0 and 16.1% surface concentration, respectively. These results suggest that both catalysts form a solid solution having strong interaction between Ni and the support. Especially, 3 and 15% Ni/Ce–ZrO_2 show 3.3 and 15.6%, respectively, which are close to bulk concentrations. These results strongly suggest that Ni can be easily incorporated into the Ce–ZrO_2 support resulting in Ni–Ce–ZrO_x solid solution.

The reducibility of support is most likely to be related with the abundance of mobile oxygen. This speculation is well supported by the estimation data of mobile oxygen in the supports or catalysts (table 5 and figure 5). Table 5 presents mobile oxygen values and figure 5 illustrates CO peak areas of the samples. The results clearly show that Ce makes more mobile oxygen when located in a Ce–ZrO_2 solid solution. $MgAl_2O_4$ does not have any mobile oxygen and MgO has small amounts of mobile oxygen (3.36 μmol/g). In the case of ZrO_2 support, it produces 5.25 μmol/g. However, the CeO_2 support makes 50 times more mobile oxygen (251.5 μmol/g) than the ZrO_2 support. Furthermore, the Ce–ZrO_2 support gives slightly higher mobile oxygen (254.7 μmol/g) than the CeO_2 support indicating that easier reducibility of Ce makes it possible to make mobile oxygen more effectively. It is noteworthy that the amount of mobile oxygen in Ce–ZrO_2 is higher than that in CeO_2. Even though CeO_2 content in Ce–ZrO_2 is only 20 wt%, mobile oxygen percentage in Ce–ZrO_2 corresponds to 77% of that in CeO_2. This result implies that the interaction between CeO_2 and ZrO_2 enhance remarkably the mobility of oxygen in either CeO_2 or ZrO_2. Besides, 3 and 15% Ni/Ce–ZrO_2 also show almost the same values of mobile oxygen as Ce–ZrO_2 without regard to the Ni incorporation. This indicates that the NiO incorporated into Ce–ZrO_2 is not hardly reduced by the H_2 reduction treatment or that once-reduced Ni is hardly oxidized by a mild oxidant such as CO_2. As shown in TPR results, free NiO species would locate on the Ni–Ce–ZrO_x interlayer surface after NiO incorporation into Ce–ZrO_2 with increasing Ni loading. While the NiO species on 3% Ni/CeZrO_2 would be hardly reduced because of the strong interaction with the support, the free NiO would be easily reduced. However, once-reduced Ni would be hardly reoxidized by CO_2. In anyway, it is confirmed that Ni/Ce–ZrO_2 can make mobile oxygen species like Ce–ZrO_2. As a consequence, Ni/Ce–ZrO_2 showed very high activities in SRM, POM, and OSRM. Mobile oxygen data are in good agreement with the OSRM reaction data. The catalysts having high mobile oxygen species showed very good activities in OSRM. For example, Ni/CeO_2 and Ni/Ce–ZrO_2 showed very high activities in OSRM, whereas Ni/CeO_2 showed low activity in SRM. In figure 5, it can be seen that CO production behavior depends on the samples. In the case of CeO_2, a relatively high CO peak was detected at the first CO_2 pulse, but it decreased fast with increasing number of pulses. However, although Ce–ZrO_2 produced 70% CO compared with CeO_2 at the first pulse, it produced more CO at the subsequent pulses. This indicates that oxygen migration is more rapid in CeO_2 than in Ce–ZrO_2. From figure 5, it is also seen that the existence of 15% Ni promotes the oxygen migration rate in contrast to 3% Ni. The free Ni species on the surface probably promotes the spillover of oxygen formed from CO_2 dissociation.

Combining the reaction results with TPR, XPS, and mobile oxygen estimation, it is deduced that the outstanding catalytic properties of Ni/Ce–ZrO_2 is owing to the trilateral interaction. The easier reducibility of Ce–ZrO_2 makes it possible to give highly mobile oxygen species *via* a redox cycle – thus enhancing decoking activity through the participation of the lattice oxygen, which subsequently would be supplemented with the oxygen from water molecules or oxygen molecules. Consequently, it results in high activity in stoichiometric SRM as well as OSRM. This suggestion is illustrated in figure 6. It is likely that the Ni/Ce–ZrO_2 catalyst is a composite of different layers. The top layer consists of relatively free Ni particles, and an intermediate layer consisting of strongly interacted Ni and Ce–ZrO_2, namely Ni–Ce–Zr–O_x, is sandwiched between the top layer and Ce–ZrO_2 support. The high oxygen storage capacity of ceria is based on the ability to store and release reversibly a large amount of oxygen, responding to the reaction condition. Ceria in the catalyst is partially reduced under reductive condition and the partially reduced ceria site produces active oxygen species from a water molecule, which reacts with the deposited carbon with the help of oxygen spillover from the support onto the Ni sites.

4. Conclusion

Ni/Ce–ZrO_2 reveals high catalytic activity as well as high stability both in SRM and OSRM compared with widely used catalytic systems such as a Ni/$MgAl_2O_4$ or Ni/MgO. The high catalyst stability is mainly ascribed to the synergistic effect of the Ce dopant resulting from strong interaction between Ni and Ce–ZrO_2, high oxygen storage capacity, and high ability to produce mobile oxygen species during the reaction.

References

[1] M.A. Peña, J.P. Gómez and J.L.G. Fierro, Appl. Catal. A 144 (1996) 7.
[2] J.N. Armor, Appl. Catal. A 176 (1999) 159.
[3] S.C. Tsang, J.B. Claridge and M.L.H. Green, Catal. Today 23 (1995) 3.
[4] A.T. Ashcroft, A.K. Cheetham, M.L.H. Green and P.D.F. Vernon, Nature 352 (1991) 225.
[5] V.R. Choudhary, A.M. Rajput and B. Prabhakar, Angew. Chem. Int. Ed. Engl. 33 (1994) 2104.
[6] X. Li, J.-S. Chang and S.-E. Park, Chem. Lett. (1999) 1099.
[7] X. Li, J.-S. Chang, M. Tian and S.-E. Park, J. Appl. Organomet. Chem. 15 (2001) 109.
[8] H.-S. Roh, W.-S. Dong, K.-W. Jun and S.-E. Park, Chem. Lett. (2001) 88.
[9] J.-S. Chang, S.-E. Park and H. Chon, Appl. Catal. A 145 (1996) 111.
[10] K.-W. Jun, K.S. Rama Rao, M.-H. Jung and K.-W. Lee, Bull. Korean Chem. Soc. 19 (1998) 466.
[11] T. Hayakawa, S. Suzuki, J. Nakamura, T. Uchijima, S. Hamakawa, K. Suzuki, T. Shishido and K. Takehira, Appl. Catal. A 183 (1999) 273.
[12] O. Yamazaki, K. Tomishige and K. Fujimoto, Appl. Catal. A 136 (1996) 49.
[13] C.-K. Loong and M. Ozawa, J. Alloy Comp. 303–304 (2000) 60.