Methane reforming over a high temperature stable-NiCoMgO$_x$ supported on zirconia–hafnia catalyst

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Abstract

The unusually high temperature stable NiCoMgO$_x$ (Ni/Co/Mg:1:0.2:1.2)/zirconia–hafnia catalyst has been investigated for syngas generation via the catalytic partial oxidation of methane (CPOM), oxidative steam reforming of methane (OSRM) and oxidative CO$_2$ reforming of methane (OCRM) processes. The catalyst, even when calcined at 1400 °C for 4 h, showed excellent activity/selectivity for the CPOM, OSRM and the OCRM reactions. On account of its high thermal stability, hot spots in the catalyst bed and/or high temperatures prevailing at the catalyst surface during the oxy-reforming processes would have little or no effect on the catalytic activity/selectivity of the NiCoMgO$_x$/zirconia–hafnia catalyst, thus making the catalyst suitable even for operating under adiabatic conditions. While the selectivity for CO increased considerably with increasing reaction temperature for the CPOM process, the selectivity for H$_2$ was affected to a much lesser extent. The selectivity for CO and H$_2$ in the CPOM reaction was found to decrease with increasing space velocity; the H$_2$ selectivity was however affected to a greater extent. For the OSRM process, the H$_2$O/CH$_4$ ratio profoundly influenced the H$_2$/CO ratio and the heat of the reaction. Depending on the H$_2$O/CH$_4$ ratio, the OSRM process could be operated in a mildly exothermic, thermoneutral or mildly endothermic mode. The CO$_2$ conversion increased rapidly with increasing OCRM temperature and correspondingly the exothermicity of the OCRM reaction was found to decrease with increasing reaction temperature. At 900 °C, the OCRM reaction was mildly exothermic and provided high methane conversion and syngas selectivity.
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1. Introduction

A major portion of the natural gas (predominantly consists of methane) reserves are located in remote or stranded areas [1]. Hence, there is a considerable interest in developing technologies that can convert methane into easily transportable liquids (gas to liquids). Syngas production (intermediate step) is a major cost for the gas to liquid processes [2]. Catalytic partial oxidation of methane (CPOM) is an attractive method for syngas generation [3–5]. However, in this process a high methane conversion (>90%) coupled with very low contact times, even at very high selectivity (>95%) for CO and H$_2$, leads to production of a large amount of heat in a small catalyst zone. This causes a large adiabatic temperature rise and ultimately results in the deactivation of a thermally unstable catalyst. Our

earlier studies showed that a highly active/selective supported Ni-containing catalyst (prepared by depositing NiO on a MgO precoated low surface area macroporous silica–alumina) was thermally stable when calcined up to ∼1000 °C; however, at a higher calcination temperature of 1200 °C it was found to deactivate completely [6]. Additionally, since the methane combustion reactions are enormously more exothermic than the partial oxidation of methane-to-syngas reaction, loss in the selectivity due to catalyst deactivation is expected to make the CPOM process hazardous. It is therefore of considerable practical interest to develop a high temperature stable catalyst, showing desirable activity and selectivity in the methane-to-syngas conversion reactions. Our preliminary studies on a NiCoMgO$_x$ catalyst deposited on a low surface area macroporous zirconia–hafnia catalyst carrier have yielded extremely promising results [7]. The NiCoMgO$_x$/SZ-5564 catalyst after high temperature calcination treatment (1400 °C) showed superior activity compared to catalysts without MgO (Table 1). Moreover, even on exposure of the catalyst to temperatures ≥2000 °C using oxy-acetylene

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Table 1
Performance comparison of supported Ni–Co (8.49 wt.% Ni and 1.73 wt.% Co) catalysts calcined at 1400 °C (for 4 h) in the partial oxidation of methane to syngas [feed: a mixture of 64.3 mol% CH_4 and 36.1 mol% O_2, GHSV = 62,000 $cm^3 g^{-1} h^{-1}$, temperature = 900 °C. All the catalysts reduced before the reaction in the presence of 50 vol.% of H_2 in N_2 at 900 °C for 2 h]

Catalyst	CH_4 conv. (%)	Selectivity (%)	
		H_2	CO
NiCoMgO$_x$/SZ-5564 (Ni/Co/Mg = 1:0.2:1.2)	98.2	96.5	96.4
NiCoO$_x$/SZ-5564 (Ni/Co = 1:0.2)	87.7	94.8	93.9
NiCoCeO$_x$/SZ-5564 (Ni/Co/Ce = 1:0.2:1.2)	92.5	96.2	93.8
NiCoZrO$_x$/SZ-5564 (Ni/Co/Zr = 1:0.2:1.2)	90.6	94.9	94.5
NiCoMgCeO$_x$/SZ-5564 (Ni/Co/Mg/Ce = 1:0.2:1.2:1.2)	98.5	96.9	96.7

flame (30 min and thermal shocks), it showed high catalytic activity/selectivity and stability in the CPOM reaction. The other MgO based catalyst in Table 1 (NiCoMgCeO$_x$/SZ-5564) is also a very promising catalysts system; detailed studies related to the NiCoMgCeO$_x$/SZ-5564 catalyst system are reported elsewhere [8].

This paper documents the effect of process parameters such as space velocity and reaction temperature on the exceptionally high temperature stable NiCoMgO$_x$/SZ-5564 catalyst. Recently, a large number of studies have also considered oxy-steam reforming (OSRM) and oxy-CO$_2$ reforming processes (OCRM) for generation of syngas [9–12]. This process is expected to be relatively non-hazardous due to the coupling of exothermic (partial oxidation of methane) and endothermic (steam reforming/CO$_2$ reforming of methane) reactions. Herein, the activity of the NiCoMgO$_x$/zirconia–hafnia catalyst has also been investigated for the oxy-steam reforming and oxy-CO$_2$ reforming processes.

2. Experimental

The supported NiCoMgO$_x$ catalyst (Ni/Co/Mg:1:0.2:1.2) was prepared by impregnating respective Ni, Co and Mg nitrates from their mixed aqueous solution on a commercial low surface area ($\cong$0.1 $m^2 g^{-1}$) macroporous (porosity = 45% and pore volume = 0.15 $cm^3 g^{-1}$) sintered zirconia–hafnia (94.1% ZrO$_2$–HfO$_2$) catalyst carrier (SZ-5564, obtained from M/s Norton Co., USA) by incipient wetness technique [7]. The catalyst was first calcined at 600 °C for 4 h and subsequently at 900 °C or 1400 °C for 4 h. The loading of Ni, Co, and MgO on the support was 8.5%, 1.7%, and 7.0%, respectively. The different phases in the catalyst were determined by XRD [7]. The TPR over the catalysts was carried out in a quartz reactor containing 0.15 g catalyst in a flow of 5 mol% H$_2$ in Ar (30 $cm^3 min^{-1}$) from 50 to 1100 °C at a linear heating rate of 20 °C min^{-1} by the procedure described earlier [7,14].

The CPOM, OSRM and OCRM reactions were carried out at atmosphere pressure in a continuous flow quartz reactor

(i.d. = 9 mm) packed with 0.2 g catalyst (22–30 mesh size) by the procedure described earlier [14]. Before use, in the reaction, the catalyst was reduced by 50% H$_2$ in N$_2$ at 900 °C for 1 h. The gas hourly space velocity (GHSV) was measured at 0 °C and 1 atm pressure. The conversion/selectivity data was obtained after attaining the reaction steady state (after a reaction period of 30 min). Some of the runs were extended for a period of 20 h. The runs showing a material balance for C, H and O with an error above 6% were rejected. The product selectivity was calculated as follows:

$$H_2 \text{ selectivity } (\%) = 100[(2 \text{ moles of } H_2 \text{ formed})/ \text{moles of } CH_4 \text{ converted}],$$

$$CO \text{ selectivity } (\%) = 100[\text{moles of CO formed}/ \text{moles of } CH_4 \text{ converted}]$$

3. Results and discussion

3.1. Catalyst characterization

XRD showed the presence of (Ni and Co–Mg) O solid solution and MgCo$_2$O$_4$ phases for the NiCoMgO$_x$ catalyst (Table 2). The XRD spectrum for the 900 °C and the 1400 °C calcined samples were similar. The temperature programmed reduction studies showed presence of two peaks. The high temperature peak with a maximum at 1045 °C was the dominant peak and was attributed to the reduction of nickel–cobalt oxides dissolved in MgO and/or doped in ZrO$_2$ of the support. The peak with maximum at 456 °C was much smaller and was related to the reduction of free Ni and/or Co oxides. The degree of reduction (estimated from the hydrogen consumed in the TPR experiments) for the NiCoMgO$_x$ catalyst was found to be ~32.8%.

3.1.1. CPOM

The influence of temperature on the CPOM performance on the NiCoMgO$_x$/SZ-5564 catalyst (precalcined at 1400 °C for 4 h) is depicted in Fig. 1. As expected the methane conversion was found to increase with increasing temperature. The conversion of oxygen was 100% at all the reaction temperatures. While the CPOM reaction is only mildly exothermic (1), the combustion side reactions ((2) and (3)), which lead to a loss in H$_2$ and CO selectivity, are highly exothermic:
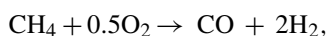
$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2,$$
$$\Delta H_{850 °C} = -5.4 \text{ kcal mol}^{-1} \tag{1}$$

Table 2
XRD and TPR characterization of NiCoMgO$_x$ catalyst deposited on a low surface area macroporous zirconia–hafnia catalyst

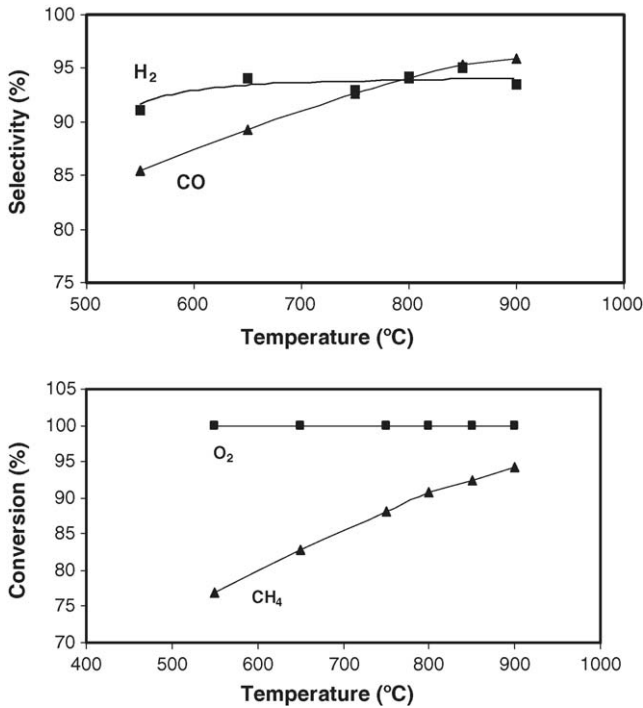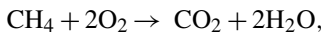| Characterization	Results
XRD phases	(Ni and Co–Mg) O solid solution and MgCo$_2$O$_4$
TPR	Peak 1 maximum: 456 °C (free Ni/Co oxide reduction)
	Peak 2 maximum: 1045 °C (metal oxide solid solutions reduction)

Fig. 1. Effect of temperature in the performance of partial oxidation of methane over NiCoMgO$_x$/SZ-5564 (precalcined at 1400 °C catalyst) [reaction condition: feed = a mixture of 64.3 mol% CH$_4$ and 35.7 mol% O$_2$; GHSV = 62,000 cm^3 g^{-1} h^{-1}].

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O,$$
$$\Delta H_{850\,°C} = -191.7\,kcal\,mol^{-1} \tag{2}$$
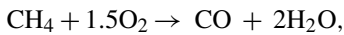
$$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O,$$
$$\Delta H_{850\,°C} = -124.3\,kcal\,mol^{-1} \tag{3}$$

Due to large differences between the exothermicity of the partial oxidation and total combustion reactions high selectivity for product H$_2$ and CO is very important for the safe operation of the CPOM process. While the selectivity for CO increased with increasing temperature, the selectivity for H$_2$ was not influenced to any significant extent. The H$_2$/CO ratio decreased from 2.2 to 2.0 as the temperature was increased from 550 to 900 °C. The H$_2$/CO ratio (value >2) cannot be explained exclusively in Eqs. (1)–(3). It is apparent that the water gas shift reaction (CO + H$_2$O → CO$_2$ + H$_2$) also plays a role in determining the selectivity of the products. The data suggests that the water gas shift (WGS) reaction occurs to a significant extent at the lower reaction temperature. With increasing reaction temperatures, reaction (1) tends to dominate and there is decreasing contribution from reaction (3) and the WGS reaction. Hence, while the H$_2$ selectivity does not increase much (Figs. 1 and 3), the CO selectivity increases considerably with temperature.

A large decrease in methane conversion was observed at 850 °C with increasing space velocity (Fig. 2); the corresponding decrease in oxygen conversion was however, very small. While the selectivity for CO and H$_2$ both decreased with increasing space velocity; the H$_2$ selectivity was affected to a greater
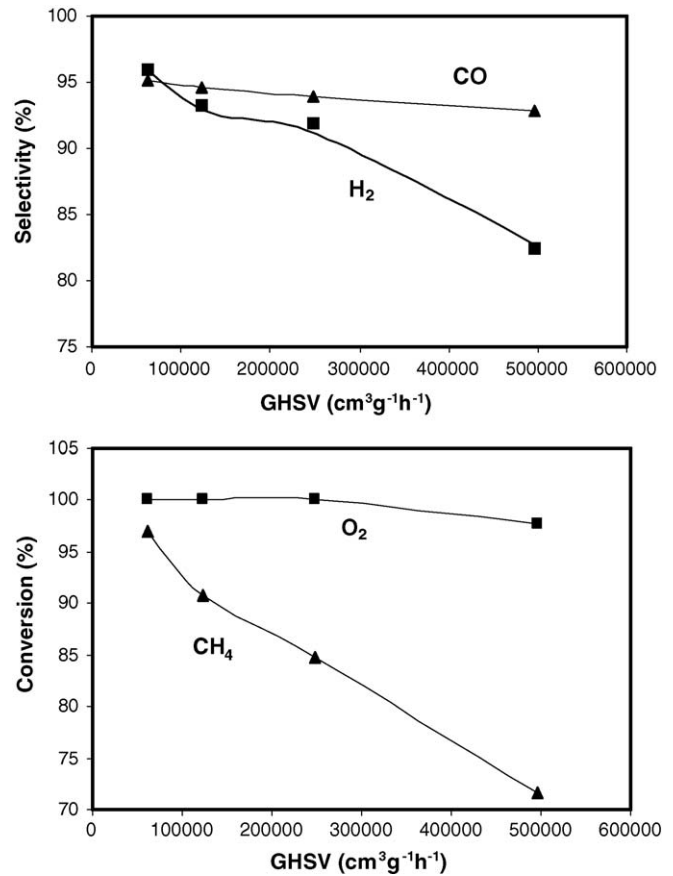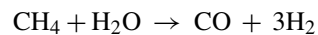

Fig. 2. Effect of GHSV in the performance of partial oxidation of methane over NiCoMgO$_x$/SZ-5564 (precalcined at 1400 °C catalyst) [reaction condition: feed = a mixture of 64.3 mol% CH$_4$ and 35.7 mol% O$_2$; reaction temperature = 850 °C].

extent. As mentioned earlier, the selectivity of H$_2$ and CO can be decreased via reactions (2) and (3). The larger decrease in the H$_2$ selectivity suggests that there is increased contribution from the methane oxidation to CO and water reaction (3) with increasing space velocity.

Temperature effect studies were also undertaken on the NiCoMgO$_x$/SZ-5564 catalyst calcined at 900 °C (Fig. 3). These studies revealed a similar behavior (trend) to that observed on the catalyst calcined at 1400 °C. A stable CPOM activity/selectivity was observed for the NiCoMgO$_x$/SZ-5564 catalyst (calcined at 1400 °C) for a 20 h period. In line with the observed absence of deactivation, no new (inactive) phase was observed in the XRD spectrum of the used catalyst.

3.1.2. OSRM

Along with the methane partial oxidation reaction (1), the steam methane reforming (SRM) and WGS (5) catalytic reactions are also important for the OSRM process:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
$$(\Delta H_{850\,°C} = +53.89\,kcal\,mol^{-1}) \tag{4}$$
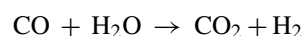
$$CO + H_2O \rightarrow CO_2 + H_2$$
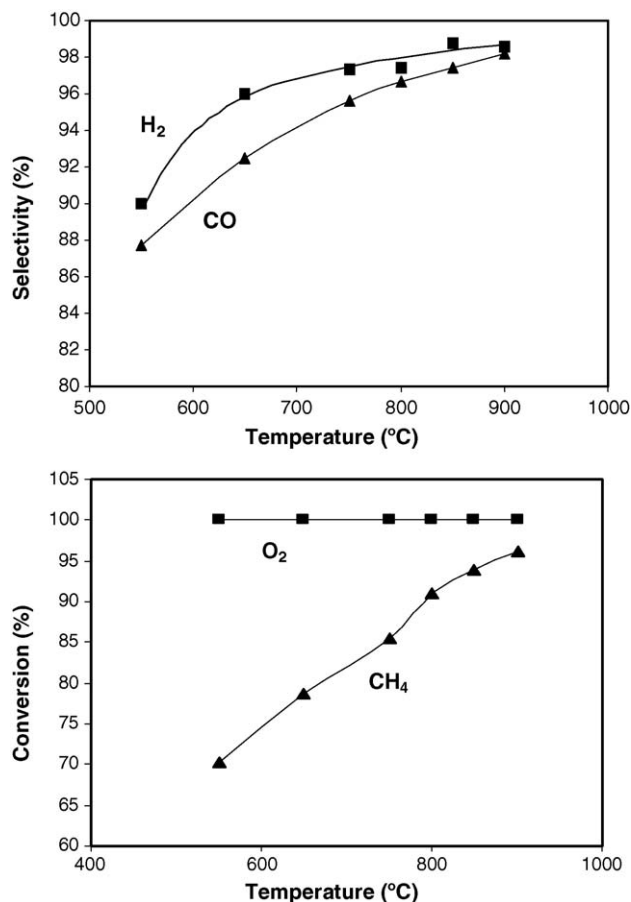$$(\Delta H_{850\,°C} = -8.04\,kcal\,mol^{-1}) \tag{5}$$

Fig. 3. Effect of temperature in the performance of partial oxidation of methane over $NiCoMgO_x$/SZ-5564 (precalcined at $900\,°C$ catalyst) [reaction condition: feed = a mixture of 64.3 mol% CH_4 and 35.7 mol% O_2; GHSV = 120,000 $cm^3\,g^{-1}\,h^{-1}$].

Results showing the influence of H_2O/CH_4 ratio in feed (when $O_2/CH_4 = 0.5$) at $850\,°C$ on the conversion, selectivity and net heat of reaction (ΔH_r) in the oxy-steam reforming of methane over the $NiCoMgO_x$/SZ-5564 catalyst (calcined at $1400\,°C$ for 4 h) are presented in Fig. 4. The O_2 was almost completely converted under all process conditions. High methane and steam conversions were also observed for the OSRM reaction; the H_2O/CH_4 ratio did not exert any appreciable influence on the methane and steam conversions. Since the conversion of water was greater than zero, the H_2 selectivity based on methane conversion was always 100%. The CO selectivity was found to decrease with increasing H_2O/CH_4. Correspondingly, the H_2/CO ratio was also found to increase from 2.2 (at $H_2O/CH_4 = 0.09$) to 2.6 (at $H_2O/CH_4 = 0.55$). The net heat of reaction (ΔH_r) for the overall process was estimated by subtracting the heat of formation (at the process temperature) of the components in the feed from that of the components in the products stream. The reaction was found to switch from mildly exothermic to moderately endothermic with increasing H_2O/CH_4 ratio. These results indicate that the OSRM process involves the simultaneous occurrence of the mildly exothermic CPOM and the moderately endothermic SRM (reaction (4)) processes; the rate of the CPOM reaction is however, expected
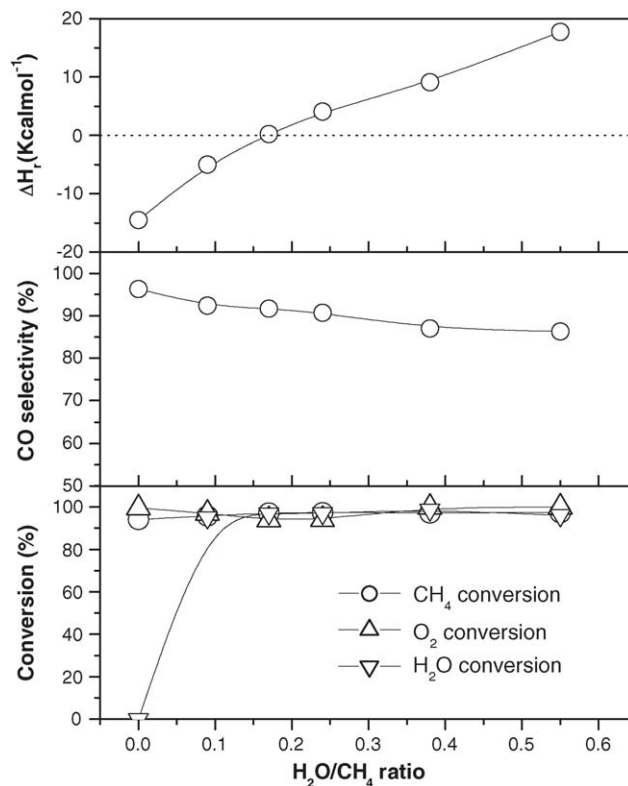

Fig. 4. Effect of H_2O/CH_4 ratio on the simultaneous POM and steam reforming of methane over $NiCoMgO_x$/SZ-55654 (calcined at $1400\,°C$) at $850\,°C$; $CH_4/[O_2 + 0.5H_2O] = 1.82$.

to be considerably higher than the SRM reaction [12,13]. As observed from Fig. 4, the CO selectivity is always lower than 100%. This deviation from 100% CO selectivity may be related to the occurrence of the complete methane combustion (2) and/or the WGS reaction (5). The increase in the H_2/CO ratio may be related to the increased participation of the SRM reaction and/or increased WGS reaction. From these studies it is apparent that the feed H_2O concentration can be utilized to tune relevant parameters such as reaction exothermicity and H_2/CO ratio for efficient syngas production on the $NiCoMgO_x$/SZ-5564 catalyst.

Similar to the CPOM studies, no change in activity/selectivity for the OSRM reaction was observed for an extended 20 h period at $900\,°C$. The high thermal stability and high catalyst activity/selectivity of the $NiCoMgO_x$/SZ-5564 catalyst makes it a very promising candidate for the OSRM reaction.

3.1.3. OCRM

The OCRM reaction was investigated over the $1400\,°C$ calcined $NiCoMgO_x$/SZ-5564 catalyst at different reaction temperatures (Fig. 5). At reaction temperatures of $900\,°C$, the catalyst showed excellent methane conversions (>90%) with high selectivity (H_2 selectivity > 90% and 100% CO_2 selectivity on the basis of methane conversion) even at a high space velocity of $46,000\,cm^3\,g^{-1}\,h^{-1}$ ($O_2/CH_4 = 2$ and $H_2O/CH_4 = 0.14$). The methane conversion and the CO_2 conversion were both found to increase with increasing reaction temperature; the reaction temperature however exerted a considerably larger influence on the
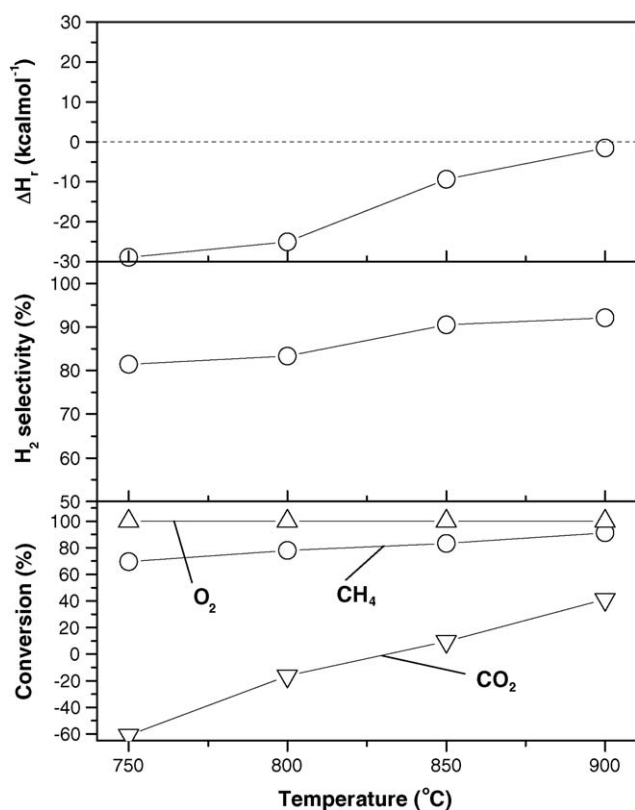
Fig. 5. Effect of temperature on the simultaneous POM and CO$_2$ reforming of methane over NiCoMgO$_x$/SZ-5564 catalyst (calcined at 1400 °C) [reaction condition: GHSV = 46,000 cm^3 g^{-1} h^{-1}; O$_2$/CH$_4$ = 0.50, CO$_2$/CH$_4$ = 0.14].

CO$_2$ conversion. The H$_2$ selectivity was also found to increase with increasing reaction temperature.

The OCRM reaction involves the coupling of the mildly exothermic CPOM reaction and the considerably endothermic CO$_2$ reforming reaction (6):

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$
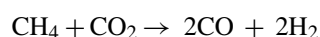
$$(\Delta H_{850 °C} = +61.03 \, \text{kcal mol}^{-1}) \tag{6}$$

At lower reaction temperatures, a negative CO$_2$ conversion is observed. This may be explained on the basis of the slow kinetics of the CO$_2$ reforming reaction. At low reaction temperatures the kinetically slow CO$_2$ reforming reaction is not expected to contribute significantly to the OCRM reaction and hence there is no consumption of CO$_2$. Instead, CO$_2$ is formed due to the complete combustion reactions of methane. The contribution from the CO$_2$ reforming reaction is expected to increase with increasing reaction temperature. This is also seen from the decrease in the exothermicity of the reaction. The OCRM reaction becomes almost thermoneutral at an OCRM reaction temperature of 900 °C. The less than 100% selectivity for H$_2$ may be related to hydrogen consumption via total combustion of methane and/or the reverse WGS reaction. The increase in H$_2$ selectivity with increasing reaction temperature is probably related to the decrease in the participation of methane in the total combustion reaction with a corresponding participation increase in the CO$_2$ reforming reaction.

OCRM time on stream studies undertaken at 900 °C, for 20 h showed no deactivation due to coking. The presence of oxygen mobility is required to keep the catalyst surface free from coke accumulation. Pulse hydrogen experiments [7] have shown that the NiCoMgO$_x$/SZ-5564 catalyst has appreciable oxygen mobility; this may be related to the doping of a part of the nickel and cobalt in ZrO$_2$ [15].

4. Concluding remarks

The salient features of the study are summarized below:

(a) NiCoMgO$_x$ supported on a commercial low surface area sintered zirconia–hafnia (94.1% ZrO$_2$–HfO$_2$) catalyst carrier showed excellent thermal stability and activity/selectivity for the CPOM, OSRM and the OCRM reactions.
(b) While the selectivity for CO increased with increasing temperature for the CPOM process, the selectivity for H$_2$ was not influenced to any significant extent.
(c) The selectivity for CO and H$_2$ in the CPOM reaction was found to decrease with increasing space velocity; the H$_2$ selectivity was however affected to a significantly greater extent; this was related to the increase contribution from the methane oxidation to CO and water reaction.
(d) The H$_2$O/CH$_4$ ratio and the reaction temperature could be used to tune the syngas H$_2$/CO ratio and the reaction exothermicity for the OSRM process; depending on the H$_2$/CH$_4$ ratio and temperature the OSRM process could be operated in a mildly exothermic, thermal neutral or mildly endothermic mode.
(e) The CO$_2$ conversion was very strongly affected by the reaction temperature; significant CO$_2$ conversion (>40%) could only be obtained at high OCRM reaction temperatures (900 °C).
(f) The exothermicity of the OCRM reaction was found to decrease with increasing reaction temperature.

References

[1] B.F. Burke, NPRA 2001 Annual Meeting (AM-01-44), March 18–20, 2001.
[2] A.P.E. York, T. Xiao, M.L.H. Green, Top Catal. 22 (2003) 345.
[3] S.S. Bhardwaj, L.D. Schmidt, Fuel Process. Technol. 42 (1995) 109.
[4] M.A. Pena, J.P. Gomez, J.L.G. Fierro, Appl. Catal. 144 (1996) 7.
[5] Y.H. Hu, E. Reckenstein, Catal. Rev. 44 (2002) 423.
[6] V.R. Choudhary, A.S. Mamman, J. Catal. 172 (1997) 281.
[7] V.R. Choudhary, K.C. Mondal, A.S. Mamman, J. Catal. 233 (2005) 36.
[8] V.R. Choudhary, K.C. Mondal, T.V. Choudhary, Appl. Catal. A: Gen. 306 (2006) 45.
[9] A.T. Ashcroft, A.K. Cheetham, M.L.H. Green, P.D.F. Vernon, Nature 352 (1991) 225.
[10] V.R. Choudhary, A.M. Rajput, B. Prabhakar, Angew Chem. Int. Edit. 33 (1994) 2104.
[11] V.R. Choudhary, A.M. Rajput, B. Prabhakar, Catal. Lett. 32 (1995) 391.
[12] W.-S. Dong, H.-S. Roh, K.-W. Jun, S.-E. Park, Y.-S. Oh, Appl. Catal. A: Gen. 226 (2002) 63.
[13] V.R. Choudhary, A.S. Mamman, B.S. Uphade, AICHE J 47 (2001) 1632.
[14] V.R. Choudhary, B.S. Uphade, A.S. Mamman, Appl. Catal. A: Gen. 168 (1998) 33.
[15] V.R. Choudhary, S. Banerjee, S.G. Pataskar, Appl. Catal. A: Gen. 253 (2003) 65.