

# High-temperature stable and highly active/selective supported NiCoMgCeO<sub>x</sub> catalyst suitable for autothermal reforming of methane to syngas

Vasant R. Choudhary\*, Kartick C. Mondal, Ajit S. Mamman

*Chemical Engineering and Process Development Division, National Chemical Laboratory, Pune 411 008, India*

## Abstract

Low-surface-area, macroporous, zirconia–hafnia-supported NiCoMgO<sub>x</sub> and NiCoMgCeO<sub>x</sub> (Ni/Co/Mg/Ce = 1/0.2/1.2/0.0 or 1.2) catalysts, precalcined at high temperature (1400 °C for 4 h), showed both high activity (> 98% conversion) and selectivity (> 95%) in the catalytic partial oxidation of methane (CPOM) to syngas. Their performance remained unchanged even after they were subjected to higher temperature (> 2000 °C for 30 min) or a number of high-temperature (> 2000 °C) shocks, due to their direct exposure to an oxyacetylene flame. The supported NiCoMgCeO<sub>x</sub>, however, showed superior performance in the steam and CO<sub>2</sub> reforming reactions because of its much higher lattice oxygen mobility. Hence it is more suitable for the autothermal reforming of methane.

© 2005-Elsevier Inc. All rights reserved.

**Keywords:** Zirconia–hafnia-supported NiCoMgO<sub>x</sub> catalyst; Zirconia–hafnia-supported NiCoMgCeO<sub>x</sub> catalysts; Catalytic partial oxidation of methane; Autothermal reforming of methane; Steam reforming of methane; CO<sub>2</sub> reforming of methane; High-temperature stable supported NiCoMgCeO<sub>x</sub> catalyst

## 1. Introduction

Methane autothermal reforming (MATR) is carried out in two separate reaction zones—in the first zone, a part of the methane from feed is combusted in a flame or catalytic burner, producing a hot (about 1400 °C) product stream, and, in the second zone, the unconverted methane from the product stream is reformed to syngas by the methane combustion products (steam and CO<sub>2</sub>) over a steam-reforming catalyst [1]. The MATR process requires no external energy, and yet its use is limited, mainly because of the catalyst fouling (deactivation by sintering and formation of inactive mixed-metal oxides and degradation/disintegration) resulting from the high-temperature (about 1400 °C) treatment and thermal shocks received by the catalyst, particularly during the process start-up and closedown periods.

In the last decade or two, extensive efforts have been made on the catalytic partial oxidation of methane (CPOM) to syngas, which is covered in a number of recent reviews [2–5]. The CPOM process, operating at a very low contact time (about a millisecond) [6–10], is of great practical importance. However, in this process a high methane conversion (> 90%) coupled with very high space velocity ( $\geq 500,000 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$ ) leads to production of a large amount of heat in a small catalyst zone, even at very high selectivity (> 95%) for CO and H<sub>2</sub>, causing a large adiabatic temperature rise (which is difficult to control) and ultimately resulting in the deactivation of a thermally unstable catalyst. Our earlier studies showed that a highly active/selective supported Ni-containing catalyst (prepared by deposition of NiO on a MgO-precoated low-surface-area macroporous silica-alumina) is thermally stable when calcined only up to about 1000 °C; at the higher calcination temperature (1200 °C), it is completely deactivated, mostly because of the formation of catalytically inactive mixed-metal oxides [11].

\* Corresponding author. Fax: +91 20 25893041.  
E-mail address: [vrc@che.ncl.res.in](mailto:vrc@che.ncl.res.in) (V.R. Choudhary).

Since the methane combustion reactions ( $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 191.8 \text{ kcal mol}^{-1}$  and  $\text{CH}_4 + \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O} + 124.1 \text{ kcal mol}^{-1}$ ) are much more exothermic than the partial oxidation of methane to syngas ( $\text{CH}_4 + 0.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 + 5.4 \text{ kcal mol}^{-1}$ ), even a small loss in the selectivity due to catalyst deactivation is expected to make the CPOM process highly hazardous, or even render it out of control. It is therefore of great practical interest to overcome the major limitation of the MATR and CPOM processes by developing a high-temperature-stable catalyst that demonstrates desirable activity and selectivity in the methane-to-syngas conversion reactions and has a high mechanical strength, even when the catalyst is subjected to a very high temperature ( $\geq 1200^\circ\text{C}$ ) and thermal shocks. This has been accomplished in this investigation. We report here that a  $\text{NiCoMgCeO}_x$  deposited on a low-surface-area macroporous zirconia–hafnia catalyst carrier, even when calcined at  $1400^\circ\text{C}$  and subjected to oxyacetylene flame (about  $2000^\circ\text{C}$ ) or subjected to a number of high-temperature (about  $2000^\circ\text{C}$ ) thermal shocks, shows high catalytic activity, selectivity, and stability in the CPOM and in the steam reforming and  $\text{CO}_2$  reforming reactions, without losing its mechanical strength. These highly desirable qualities are of great practical importance for use of the catalyst in the MATR process and in the high-temperature CPOM process.

## 2. Experimental

The supported  $\text{NiCoO}_x$  ( $\text{Ni}/\text{Co} = 1:0.2$ ),  $\text{NiCoCeO}_x$  ( $\text{Ni}/\text{Co}/\text{Ce} = 1:0.2:1.2$ ),  $\text{NiCoMgO}_x$  ( $\text{Ni}/\text{Co}/\text{Mg} = 1:0.2:1.2$ ), and  $\text{NiCoMgCeO}_x$  ( $\text{Ni}/\text{Co}/\text{Mg}/\text{Ce} = 1:0.2:1.2:1.2$ ) catalysts were prepared by the impregnation of respective metal nitrates from their mixed aqueous solution on a commercial low-surface-area ( $\cong 0.1 \text{ m}^2 \text{ g}^{-1}$ ) macroporous (porosity = 45% and pore volume =  $0.15 \text{ cm}^3 \text{ g}^{-1}$ ) sintered zirconia–hafnia (94.1%  $\text{ZrO}_2$ – $\text{HfO}_2$ ) catalyst carrier (SZ-5564, obtained from M/S Norton Co., USA) by the incipient wetness technique and calcination first at  $600^\circ\text{C}$  for 4 h and then at  $900$  or  $1400^\circ\text{C}$  for 4 h. The loading of Ni and Co with or without  $\text{CeO}_2$  and/or  $\text{MgO}$  on the support was as follows: 8.5% Ni and 1.7% Co for the  $\text{NiCoO}_x/\text{SZ-5564}$ ; 8.5% Ni, 1.7% Co, and 30.1%  $\text{CeO}_2$  for the  $\text{NiCoCeO}_x/\text{SZ-5564}$ ; 8.5% Ni, 1.7% Co, and 7.0%  $\text{MgO}$  for the  $\text{NiCoMgO}_x/\text{SZ-5564}$ ; and 8.5% Ni, 1.7% Co, 7.0%  $\text{MgO}$ , and 30.1%  $\text{CeO}_2$  for the  $\text{NiCoMgCeO}_x/\text{SZ-5564}$ . To ascertain the presence of different metal oxides and/or mixed-metal oxide phases, we characterized the catalysts by XRD.

The high-temperature (about  $2000^\circ\text{C}$ ) treatment of the catalysts and the temperature shocks were accomplished by the application of an oxyacetylene flame (oxidizing portion of the flame) directly to the catalyst (0.3 g), which was kept in a zirconia boat once for 30 min or repeatedly (six times) for 30 s at intervals of 10 min.

The CPOM and steam and  $\text{CO}_2$  reforming reactions over the catalysts were carried out at atmospheric 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 [11–13]. Before use, in the reaction, the catalyst was reduced by 50%  $\text{H}_2$  in  $\text{N}_2$  at  $900^\circ\text{C}$  for 1 h. The gas hourly space velocity (GHSV) was measured at  $0^\circ\text{C}$  and 1 atm pressure.

The TPR over the catalysts was carried out in a quartz reactor containing 0.15 g catalyst in a flow of 5 mol%  $\text{H}_2$  in Ar ( $30 \text{ cm}^3 \text{ min}^{-1}$ ) from  $50$  to  $1100^\circ\text{C}$  at a linear heating rate of  $20^\circ\text{C min}^{-1}$  by the procedure described earlier [11]. The  $\text{H}_2$  pulse reaction over the catalysts was carried out in a quartz pulse microreactor (containing 0.1 g catalyst) connected to a gas chromatograph [14] (with a porapak-Q column and thermal conductivity detector) by injection of a pulse of pure  $\text{H}_2$  ( $0.2 \text{ cm}^3$ ) in the reactor, with Ar as the carrier gas, at different temperatures ( $200$ – $900^\circ\text{C}$ ) or the injection at  $900^\circ\text{C}$  of a number of  $\text{H}_2$  pulses, one after another, at an intervals of 10 min or 1 h, after which the conversion of  $\text{H}_2$  in each pulse experiment was determined.

## 3. Results and discussion

Results for the CPOM over the zirconia–hafnia-supported  $\text{NiCoO}_x$ ,  $\text{NiCoCeO}_x$ ,  $\text{NiCoZrO}_x$ ,  $\text{NiCoMgO}_x$ ,  $\text{NiCoMgCeO}_x$ , and  $\text{NiCoMgZrO}_x$  catalysts are listed in Table 1. The crystalline metal oxides and/or mixed-metal oxide phases present on the support for the supported catalysts are also included in Table 1. The results indicate that the catalyst containing  $\text{MgO}$  with or without cerium oxide showed very high methane conversion activity ( $> 98\%$  methane conversion) and high selectivity for both CO and  $\text{H}_2$  ( $> 96\%$ ) in the CPOM process at a low contact time ( $\text{GHSV} = 62,000 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$ ), even when the catalysts were precalcined at a very high temperature ( $1400^\circ\text{C}$ ). It is interesting to note that when all of these catalysts were supported on alumina, silica, or silica-alumina support and calcined at the high temperature, they showed little or no activity in the CPOM process because of the formation of catalytically inactive mixed-metal oxide phases by the solid–solid reaction between the catalytically active components (viz., Ni and Co) with silica and/or alumina [11, 15]. In the present case, even the supported  $\text{NiCoO}_x$  catalyst with or without  $\text{CeO}_2$  or  $\text{ZrO}_2$ , calcined at a temperature as high as  $1400^\circ\text{C}$ , shows high activity and selectivity in the CPOM process. This is attributed to the fact that the support (zirconia–hafnia) does not react with the catalytically active components during the high-temperature catalyst calcination. Among the supported catalysts (Table 1), the supported  $\text{NiCoMgO}_x$  and  $\text{NiCoMgCeO}_x$  catalysts are highly promising.

To further confirm their high-temperature stability, the two promising catalysts ( $\text{NiCoMgO}_x/\text{SZ-5564}$  and  $\text{NiCoMgCeO}_x/\text{SZ-5564}$ ) were further subjected to very high-temperature ( $> 2000^\circ\text{C}$ ) shocks by direct exposure to an oxyacetylene flames for different periods, and their performance in the CPOM process was evaluated; the results

Table 1

Performance of the supported Ni–Co catalysts (with or without MgO and/or CeO<sub>2</sub>) calcined at 1400 °C (for 4 h) in the partial oxidation of methane to syngas (feed = a mixture of 64.3 mol% CH<sub>4</sub> and 35.7 mol% O<sub>2</sub>, GHSV = 62,000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup> and temperature = 900 °C)

Catalyst	XRD phases	Conversion (%)		Selectivity (%)	
		CH <sub>4</sub>	O <sub>2</sub>	H <sub>2</sub>	CO
NiCoO <sub>x</sub> /SZ-5564	NiO, CoO, Co <sub>2</sub> O <sub>3</sub> and Co <sub>3</sub> O <sub>4</sub>	87.7	100	94.8	93.9
NiCoZrO <sub>x</sub> /SZ-5564	–	90.6	100	94.9	94.5
NiCoCeO <sub>x</sub> /SZ-5564	–	92.5	100	96.2	93.8
NiCoMgO <sub>x</sub> /SZ-5564	NiO–MgO and CoO–MgO solid solutions and MgCo <sub>2</sub> O <sub>4</sub>	98.2	100	96.5	96.4
NiCoMgCeO <sub>x</sub> /SZ-5564	NiO–MgO and CoO–MgO solid solutions, MgCo <sub>2</sub> O <sub>4</sub> , MgCeO <sub>3</sub> and CeO <sub>2</sub>	98.5	100	96.9	96.7
NiCoMgZrO <sub>x</sub> /SZ-5564	–	92.6	100	96.5	95.4

Table 2

Performance of the NiCoMgO<sub>x</sub>/SZ-5564 and NiCoMgCeO<sub>x</sub>/SZ-5564 catalysts (precalcined at 900 or 1400 °C), subjected to high temperature shocks by directly exposing them to acetylene-oxygen flame, in the partial oxidation of methane to syngas at 850 °C (feed = a mixture of 64.3 mol% CH<sub>4</sub> and 35.7 mol% O<sub>2</sub>)

Catalyst pre-calcination temperature (°C)	Time for exposure to the flame (min)	GHSV (cm <sup>3</sup> g <sup>-1</sup> h <sup>-1</sup> )	Conversion (%)		Selectivity (%)	
			CH <sub>4</sub>	O <sub>2</sub>	CO	H <sub>2</sub>
Catalyst: NiCoMgO <sub>x</sub> /SZ-5564						
900	None	120,000	95.7	100	97.4	98.4
900	30 (once)	120,000	95.6	100	96.1	98.0
1400	15 (once)	62,000	95.6	100	97.4	97.8
1400	30 (once)	62,000	95.5	100	98.5	98.4
1400	0.5 (six times) <sup>a</sup>	62,000	95.8	100	97.6	98.6
Catalyst: NiCoMgCeO <sub>x</sub> /SZ-5564						
900	None	62,000	97.5	100	97.1	97.1
900	15 (once)	120,000	98.3	100	96.9	96.7
900	30 (once)	120,000	98.2	100	96.7	98.2
900	0.5 (six times) <sup>a</sup>	120,000	96.9	100	97.2	98.4
1400	30 (once)	62,000	97.2	100	96.9	97.6

<sup>a</sup> The catalyst was exposed to the oxy-acetylene flame repeatedly after an interval of 10 min, during which the flame-exposed catalyst is suddenly cooled in a flow of cool air. Thus the catalyst was subjected to high temperature shocks.

are listed in Table 2. Even when the NiCoMgO<sub>x</sub>/SZ-5564 and NiCoMgCeO<sub>x</sub>/SZ-5564 catalysts were subjected to the higher temperature ( $\geq 2000$  °C) for 30 min or high-temperature ( $\geq 2000$  °C) shocks (from direct exposure to an oxyacetylene flame), both catalysts showed almost no change in their activity and selectivity in the CPOM process (Table 2). After the high-temperature thermal treatments, neither any disintegration of the catalyst particles nor any loss in their mechanical strength/attrition resistance was observed. Thus, both catalysts show very high thermal stability for their use in the CPOM process, and their performances in the CPOM process are quite comparable. However, when the two catalysts (precalcined at 1400 °C) are compared for their performance in the methane steam and CO<sub>2</sub> reforming reactions (Table 3), the supported NiCoMgO<sub>x</sub> catalyst showed very poor performance as compared with that showed by the supported NiCoMgCeO<sub>x</sub> catalyst. The latter catalyst showed high activity in the steam reforming (94.2% methane conversion) and good CO<sub>2</sub> reforming activity (75% methane conversion) at a space velocity (GHSV = 20,000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup>) much higher than that normally used in the commercial steam reforming process.

Table 3

Performance of the NiCoMgO<sub>x</sub>/SZ-5564 and NiCoMgCeO<sub>x</sub>/SZ-5564 catalysts calcined at 1400 °C (for 4 h) in the methane steam and CO<sub>2</sub> reforming reactions at 850 °C [GHSV = 20,000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup>]

Catalyst	Methane conversion (%)	Selectivity (%)	
		H <sub>2</sub>	CO
Steam reforming of methane (feed = 25 mol% CH <sub>4</sub> and 75 mol% steam)			
NiCoMgO <sub>x</sub> /SZ-5564	78.8	100	61.9
NiCoMgCeO <sub>x</sub> /SZ-5564	94.2	100	64.0
CO <sub>2</sub> reforming of methane (feed = 47.6 mol% CH <sub>4</sub> and 52.4 mol% CO <sub>2</sub> )			
NiCoMgO <sub>x</sub> /SZ-5564	29.4	90.7	100
NiCoMgCeO <sub>x</sub> /SZ-5564	74.7	97.3	100

The above results clearly indicate that both the supported NiCoMgO<sub>x</sub> and NiCoMgCeO<sub>x</sub> catalysts have very high-thermal stability against the high-temperature treatments/thermal shocks, and both show high activity and selectivity in the CPOM process. Both catalysts also showed stable activity and selectivity when their performance in the CPOM process was tested for 50 h. Because of their high-thermal stability, the formation of hot spots in the catalyst bed and/or high temperatures prevailing at the catalyst sur-

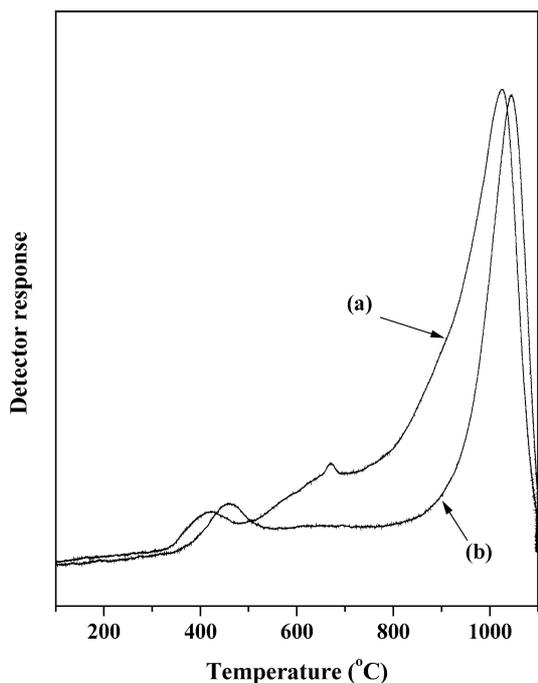


Fig. 1. Temperature programmed reduction (TPR) by  $H_2$  of  $NiCoMgCeO_x/SZ-5564$  (a) and  $NiCoMgO_x/SZ-5564$  (b).

face during the CPOM process would cause little or no effect on the catalytic activity and selectivity of the two catalysts, making them suitable for the CPOM process, even under adiabatic conditions. These results also indicate that there is little or no formation of catalytically inactive mixed-metal oxide phases during the high-temperature treatments of both catalysts. However, for the MATR process, the supported  $NiCoMgCeO_x$  catalyst is more suitable than the supported  $NiCoMgO_x$  catalyst, because of the much higher performance of the former catalyst in both the steam and  $CO_2$  reforming reactions. However, neither catalyst showed deactivation due to coking for 20 h, even for  $CO_2$  reforming. This is consistent with our earlier studies indicating that the presence of cobalt in the nickel-containing catalysts causes a drastic reduction in the coke formation in the oxidative conversion [12,15,16], oxy- $CO_2$  reforming [17], and  $CO_2$  reforming [13,17] of methane to syngas.

The much higher activity observed in both the steam and  $CO_2$  reforming reactions of the supported  $NiCoMgCeO_x$  catalyst (Table 3) is attributed mostly to its higher oxygen storage capacity and/or oxygen mobility because of the presence of cerium oxide in the catalyst, as indicated by the temperature-programmed reduction (TPR) by  $H_2$  (Fig. 1) and also by the  $H_2$  pulse reaction (Fig. 2) over the two catalysts.

The TPR curve for the supported  $NiCoMgO_x$  catalyst shows two TPR peaks (with maxima at 456 and 1045 °C), whereas that for the supported  $NiCoMgCeO_x$  catalyst shows three peaks (with peak maxima at 413, 670, and 1027 °C) (Fig. 1). For both catalysts, the first low-temperature peak (between 300 and 500 °C) is due to the reduction of free

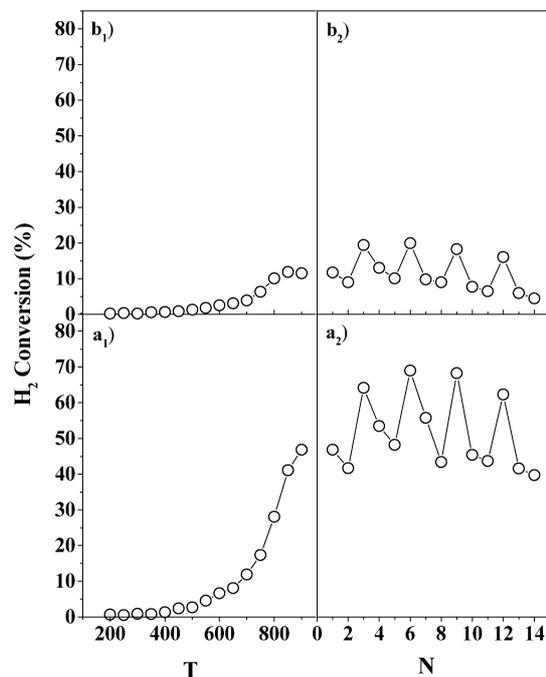


Fig. 2.  $H_2$  conversion ( $X_{H_2}$ ) in the pulse reaction of pure  $H_2$  over the  $NiCoMgCeO_x/SZ-5564$  (a<sub>1</sub>, a<sub>2</sub>) and  $NiCoMgO_x/SZ-5564$  (b<sub>1</sub>, b<sub>2</sub>) catalysts (both precalcined at 1400 °C) as a function of reaction temperature ( $T$ ) or pulse number ( $N$ ) at 900 °C. For studying the influence of pulse number on the  $H_2$  conversion, each of the  $H_2$  pulses numbered 1, 2, 4, 5, 7, 8, 10, 11, 13 and 14 was injected in the reactor at 900 °C after an interval of 10 min, whereas each of the  $H_2$  pulses numbered 3, 6, 9 and 12 was injected after an interval of 1.0 h.

nickel and/or cobalt oxides and that at the high temperatures (above 800 °C) corresponds to the reduction of nickel–cobalt oxides dissolved in the MgO and doped in the  $ZrO_2$  (from the support). The peak between 500 and 700 °C for the supported  $NiCoMgCeO_x$  catalyst is expected mostly because of the reduction of cerium oxide ( $2CeO_2 + H_2 \rightarrow Ce_2O_3 + H_2O$ ) present at the catalyst surface [18]. The XPS of this catalyst showed that the surface concentration of cerium is much lower than that of the magnesium in the catalyst (at the surface  $Ce/Mg = 0.02$ ). This is expected because of the formation of  $CeO_2-ZrO_2$  (from the support) solid solution at the high calcination temperature. The degree of reduction of the nickel and cobalt oxides (estimated from the  $H_2$  consumed in the TPR) is found to be 32.8 and < 55.2%, respectively, for the supported  $NiCoMgO_x$  and  $NiCoMgCeO_x$  catalysts.

The very significant shift observed in the TPR curve for the supported  $NiCoMgCeO_x$  catalyst toward the lower temperature side (Fig. 1) and the higher degree of reduction clearly show that the reduction of the nickel and cobalt oxides of the supported catalyst becomes easier because of the presence of cerium oxide in the catalyst. This is expected mostly because of an increase in the mobility of lattice oxygen in the catalyst in the presence of cerium oxide, particularly in the form of  $MgCeO_3$  (observed by XRD) and  $CeO_2-ZrO_2$  solid solution.

Results of the H<sub>2</sub> pulse reaction over both catalysts at different temperatures and as a function of pulse number (at 900 °C) (Fig. 2) further confirm the above conclusion/prediction. In the case of the supported NiCoMgCeO<sub>x</sub> catalyst, the H<sub>2</sub> conversion (at the same temperature) in the pulse reaction is much higher (Fig. 2a<sub>1</sub>, b<sub>1</sub>) and the observed increase in the H<sub>2</sub> conversion for the H<sub>2</sub> pulse injected after a much longer period (1 h) is also much higher (Fig. 2a<sub>2</sub>, b<sub>2</sub>). The increase in the H<sub>2</sub> conversion (by about 10 and 20% for the supported NiCoMgO<sub>x</sub> and NiCoMgCeO<sub>x</sub>, respectively) due to the increase in the interval for the H<sub>2</sub> pulse injection (from 10 min to 1 h) is attributed to the migration of subsurface oxygen to the catalyst surface. These results clearly showed that the lattice oxygen in the catalyst in the presence of cerium oxide is more mobile. Thus the presence of cerium oxide in the catalyst not only provides an oxygen storage capacity, but also greatly enhances the mobility of lattice oxygen in the catalyst. Hence, the supported NiCoMgCeO<sub>x</sub> catalyst, even when calcined at 1400 °C, shows excellent performance not only in the CPOM but also in the steam and CO<sub>2</sub> reforming reactions, with high stability against deactivation due to coking, even in the CO<sub>2</sub> reforming. The appreciable oxygen mobility observed in the supported NiCoMgO<sub>x</sub> catalyst is expected, however, because of the doping of a part of the nickel and cobalt in the ZrO<sub>2</sub> [19,20].

#### 4. Conclusions

Low-surface-area, macroporous, zirconia–hafnia-supported NiCoMgCeO<sub>x</sub> (Ni/Co/Mg/Ce = 1/0.2/1.2/1.2) catalyst shows high catalytic activity, selectivity, and mechanical stability when it is calcined at a very high temperature (at 1400 °C for 4 h or > 2000 °C for 0.5 h) or even when it is subjected to a number of high-temperature (> 2000 °C) shocks. Because of its high catalytic activity and selectivity and excellent thermal stability, this catalyst is particularly suitable for the autothermal reforming of methane to syngas, involving the exposure of catalyst to high temperatures and/or high-temperature thermal shocks. In the absence of CeO<sub>2</sub> the catalyst also shows similar high-temperature stability and a comparable activity and selectivity in the CPOM process, but it shows a markedly inferior performance in

the steam and CO<sub>2</sub> reforming reactions. The better performance of the former catalyst in the steam and CO<sub>2</sub> reforming reactions is due to the presence of cerium oxide, which not only provides an oxygen storage capacity, but also greatly enhances the mobility of lattice oxygen in the catalyst.

#### Acknowledgments

K.C. Mondal is grateful to the University Grand Commission, New Delhi, India, for the award of the senior research fellowship. The authors are grateful to Dr. Mirejkar and Dr. A.B. Mandale (both from NCL, Pune) for their help in obtaining TPR and XPS data.

#### References

- [1] Ulmann's Encyclopedia of Industrial Chemistry, vol. A12, fifth ed., VCH, Weinheim, 1989, p. 169.
- [2] S.S. Bhardwaj, L.D. Schmidt, *Fuel Process. Technol.* 42 (1995) 109.
- [3] M.A. Pena, J.P. Gomez, J.L.G. Fierro, *Appl. Catal.* 144 (1996) 7.
- [4] S.C. Tsang, J.B. Claridge, M.L.H. Green, *Catal. Today* 23 (1995) 3.
- [5] Y.H. Hu, E. Ruckenstein, *Catal. Rev.* 44 (3) (2002) 423.
- [6] V.R. Choudhary, A.S. Mamman, S.D. Sansare, *Angew. Chem. Int. Ed. Engl.* 31 (9) (1992) 1189.
- [7] V.R. Choudhary, A.M. Rajput, V.H. Rane, *J. Phys. Chem.* 96 (1992) 8686.
- [8] V.R. Choudhary, A.M. Rajput, V.H. Rane, *Catal. Lett.* 16 (1992) 269.
- [9] D.A. Hickman, L.D. Schmidt, *Science* 259 (1993) 343.
- [10] D.A. Hickman, E.A. Hauptfear, L.D. Schmidt, *J. Catal.* 138 (1992) 267.
- [11] V.R. Choudhary, A.S. Mamman, *J. Catal.* 172 (1997) 281.
- [12] V.R. Choudhary, V.H. Rane, A.M. Rajput, *Appl. Catal. A: Gen.* 162 (1997) 235.
- [13] V.R. Choudhary, A.S. Mamman, B.S. Uphade, R.E. Babcock, in: C. Song, A.F. Gaffney, K. Fujimoto (Eds.), *CO<sub>2</sub> Conversion and Utilization*, ACS, Washington, DC, 2001, p. 224.
- [14] V.R. Choudhary, V.H. Rane, *J. Catal.* 135 (1992) 310.
- [15] V.R. Choudhary, B.S. Uphade, A.S. Mamman, *Catal. Lett.* 32 (1995) 387.
- [16] V.R. Choudhary, A.M. Rajput, Prabhakar, A.S. Mamman, *Fuel* 77 (1998) 1803.
- [17] V.R. Choudhary, A.S. Mamman, *J. Chem. Technol. Biotech.* 73 (1998) 345.
- [18] V.R. Choudhary, S. Banerjee, S.G. Pataskar, *Appl. Catal. A: Gen.* 253 (2003) 65.
- [19] R. de Souza Monteiro, F.B. Noronha, L.C. Dieguez, M. Schmal, *Appl. Catal.* 131 (1995) 89.
- [20] W.-S. Dong, H.-S. Roh, K.-W. Jun, S.-E. Park, Y.-S. Oh, *Appl. Catal. A: Gen.* 226 (2002) 63.