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Carbon-free dry reforming of methane to syngas over $NdCoO_3$ perovskite-type mixed metal oxide catalyst

Vasant R. Choudhary*, Kartick C. Mondal, Ajit S. Mamman, and Upendra A. Joshi

Chemical Engineering and Process Development Division, National Chemical Laboratory, Pune, 411008

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$CoNdO_x$ (Co/Nd = 1) is a highly promising catalyst for the carbon-free CO_2 reforming of methane. Influence of the Co/Nd ratio on the catalyst performance in the CO_2 reforming and also on the crystalline phases and reduction by temperature programmed reduction (TPR) of the $CoNdO_x$ catalyst has also been investigated. The $CoNdO_x$ (CoNd = 1.0) catalyst consisted of mainly $NdCoO_3$ perovskite-type mixed metal oxide and it showed not only a high resistance to carbon formation at different process conditions (*viz*. temperature = 750–900 °C and gas hourly space velocity (GHSV) = 10000–50000 $cm^3 g^{-1} h^{-1}$) but also high activity and selectivity in the CO_2 reforming process. The high resistance to carbon formation for this catalyst is attributed mostly to strong metal (Co°)–support (Nd_2O_3) interactions.

KEY WORDS: CO_2 reforming of methane to syngas; $CoNdO_x$ catalyst; $NdCoO_3$ perovskite; resistance to carbon formation in CO_2 reforming.

1. Introduction

Carbon dioxide is a green house gas. The present global warming has been attributed to a large increase in the CO_2 concentration in the atmosphere [1,2]. Environmental concerns over the increasing CO_2 concentration have recently driven the interest of CO_2 conversion particularly for the production of syngas by CO_2 reforming (commonly called as dry reforming) of methane [2,4]. Since, the last few years, the research activities on the CO_2 reforming have gained a lot of momentum. Recent studies showed use of a number of catalysts for the CO_2 reforming of methane, *viz*. NiO–CaO [5], NiO–MgO [6,7], Ni–Co–MgO [7], NiO or $Ni_{1-x}Co_xO$/MgO/SA-5205 [8,9] Ni/ZrO_2 [10], Ni or Co/Al_2O_3 [11], Co/MgO [12] and supported Pt [13], Rh [14] and Ru or Ir [15] catalysts. A very serious problem associated with the CO_2 reforming of methane is a rapid carbon deposition on the catalyst. In general, the rate of carbon deposition is very high for the Ni-based catalysts and relatively slower for the Co- and noble metal based catalysts. Carbon formation in the CO_2 reforming results mainly by carbon monoxide disproportionation ($2CO \longrightarrow CO_2 + C$ and/or methane decomposition ($CH_4 \longrightarrow C + 2H_2$) reactions. Efforts have been made earlier for reducing the carbon formation by carrying out CO_2 reforming in the presence of steam [5,7,9] or oxygen [7,8,16,17] or both [7,17,18]. Addition of cobalt [7,9,17] or alkali metal oxide [19] to nickel catalyst has also been found to suppress the carbon formation in the CO_2 reforming. However, in spite of all these efforts, the rapid coking catalyst remained as a major problem in the CO_2 reforming process. Unless the carbon formation is eliminated or drastically reduced, this process cannot be practiced commercially. It is, therefore, of great practical importance to develop a catalyst, which does not allow carbon formation in the CO_2 reforming.

In this paper, we report the use of a novel catalyst, $CoNdO_x$ containing mainly $NdCoO_3$ perovskite-type mixed metal oxide, which shows high activity for the CO_2 reforming of methane without carbon deposition on the catalyst. A number of other Ni, Co and/or noble metal containing catalysts have also been compared for their performance in the CO_2 reforming. Influence of Co/Nd ratio and process conditions on the performance of $CoNdO_x$ (Co/Nd = 1.0) in the carbon-free CO_2 reforming has been investigated.

2. Experimental

The Rh (5.0 wt%)/$A1_2O_3$ and Ru (5.0 wt%)/$A1_2O_3$ catalysts were obtained from Lancaster (England). The Ni or Co containing mixed metal oxide catalysts (table 1) were prepared by mixing nickel or cobalt nitrate with corresponding metal oxide in the required mole ratio in the presence of deionized water such that a thick paste is formed, drying the paste and then calcining it at 900 °C for 4 h and crushing the catalyst mass to 30–60 mesh size particles.

The $CoNdO_x$ (Co/Nd = 0.1–4.0) catalysts were characterized by X-ray diffraction and temperature

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* To whom correspondence should be addressed.
E-mail: vrc@ems.ncl.res.in

Table 1

Results of the CO_2 reforming of Methane over different Ni-, Co-or noble metal-containing catalysts at 850 °C (feed: a mixture of CH_4 and CO_2 (47.5 mol% CH_4), GHSV = 20,000 $cm^3\ g^{-1}\ h^{-1}$ and time-on-stream = 15 ± 2 h)

Catalyst	CH_4 Conversion (%)	H_2 Selectivity (%)	H_2/CO ratio	Rate of carbon deposition[b] $^{\times 0\hat{}3}$ [g(C)/g(cat)]/h	TOFc (mmol $g^{-1}\ h^{-1}$)
$CoMgO_x$ (Co/Mg = 1.0)[a]	No reaction	–	–	–	–
$CoCaO_x$ (Co/Ca = 1.0)[a]	< 5	–	–	–	< 21
$NiMgO_x$ (Ni/Mg = 1.0)	98.0	97.9	0.94	1.83	413.1
$CoO_x/A1_2O_3$ (Co/Al = 1.0)	77.3	94.7	0.86	1.01	325.9
CoO_x–ZrO_2 (Co/Zr = 1.0)	98.1	93.5	0.95	0.48	413.5
CoO_x–ThO_2 (Co/Th = 10)	84.3	94.7	0.86	0.15	355.4
CoO_x–Y_2O_3 (Co/Y = 1.0)	93.0	93.8	0.92	0.61	392.0
$CoLaO_x$ (Co/La = 1.0)	26.0	55.5	0.38	1.53	109.6
$CoSmO_x$ (Co/Sm = 1.0)	34.2	60.5	0.45	1.12	144.2
$CoCeO_x$ (Co/Ce = 1.0)	94.1	99.8	0.91	0.35	396.7
$CoEuO_x$ (Co/Eu = 1.0)	13.0	51.7	0.35	0.12	54.8
$CoYbO_x$ (Co/Yb = 1.0)	30.5	60.1	0.45	0.51	128.6
Rh (5 wt%)/Al_2O_3	97.7	94.0	0.94	0.25	411.9
Ru (5 wt%)/Al_2O_3	97.8	97.9	0.96	0.57	412.3
$CoNdO_x$ (Co/Nd = 1.0)	92.3	95.5	0.91	0.00	389.1

[a] With or without reduction by H_2 at 800 ° or 900 °C for 1 h.

[b] Mass of carbon deposited per unit mass of catalyst per hour.

[c] Turnover frequency, defined as the amount of methane converted per unit mass of catalyst per hour.

programmed reduction in a flow of 5.0 mol% H_2 in Ar at a linear heating rate of 10 °C/min from 100 to 800 °C, using a thermal conductivity detector. The catalyst in its active form (i.e. after the reaction) was also characterized by X-ray photoelectron spectroscopy.

The CO_2 reforming reaction over the catalysts was carried out at atmospheric pressure by passing continuously, a gaseous feed containing pure methane and carbon dioxide (CO_2/CH_4 mole ratio = 1.1) over the catalyst (0.3 g) packed in a quartz tubular reactor (i.d. = 9 mm), provided with a thermocouple in the catalyst bed, at different GHSVs (gas hourly space velocity, measured at °C, and 1 atm pressure) and temperatures. After attaining the reaction steady state, the reaction products were analyzed by a gas chromatograph with thermal conductivity detector using a Spherocarb column. The carbon deposited on the catalyst during the reaction for a period of 15 ± 2 h was determined by oxidizing it to CO_2 in a flow of air (60 cm^3/min) for a period of 2 h at 800 °C and measuring quantitatively the amount of CO_2 produced by absorbing it in barium hydroxide solution forming barium carbonate, which was then estimated gravimetrically.

3. Results and discussion

A number of important nickel, cobalt or noble metal containing catalysts have been evaluated for their performance in the CO_2 reforming and the results, are presented in table 1. The $NiMgO_x$, CoO_x–ZrO_2, CoO_x–Y_2O_3, $CoCeO_x$ and Rh or Ru/Al_2O_3 catalysts showed high activity (methane conversion > 90%) and also high H_2-selectivity (> 94%) but with high rate of carbon deposition on them during the reaction. However, there was no carbon formation observed in the reaction when the $CoNdO_x$ (Co/Nd = 1.0) was used as the CO_2 reforming catalyst. Moreover, this catalyst also showed not only high activity (methane conversion = 92.3%) with high H_2 selectivity (95.5%) at a high space velocity (20,000 $cm^3\ g^{-1}\ h^{-1}$) but also high stability against the catalyst deactivation in the process (figure 1). All these qualities make this catalyst practically very promising for the CO_2 reforming process. During the initial CO_2 reforming period (up to 6 h), the $CoNdO_x$ catalyst is reduced, first by the methane from the feed and then by the H_2 and CO produced in the reforming of methane over the partially reduced catalyst. Consequently, both the activity and H_2 selectivity in the reforming over the catalyst are increased with the time in the initial short reaction period (upto about 6 h) and then remained constant for further period. After the initial reaction period, there was no change in the methane conversion and H_2 selectivity, when the reaction was carried out for 60 h (figure 1). However, when the catalyst was prereduced by hydrogen (5% H_2/N_2 mixture), there was no effect of time on the conversion and selectivity in the initial reaction period. The catalyst in its active form is essentially a highly dispersed metallic cobalt on Nd_2O_3.

Results showing the influence of Co/Nd mole ratio of the catalyst on its performance in the dry reforming process are presented in figure 2. A Co/Nd ratio of 1.0 has been found to be the optimum ratio for the catalyst for its best performance. However, for all these $CoNdO_x$ catalysts, there was no carbon formation in the CO_2 reforming.

The $CoNdO_x$ (Co/Nd = 0.1–4.0) catalysts were characterized for crystalline phases and also by their

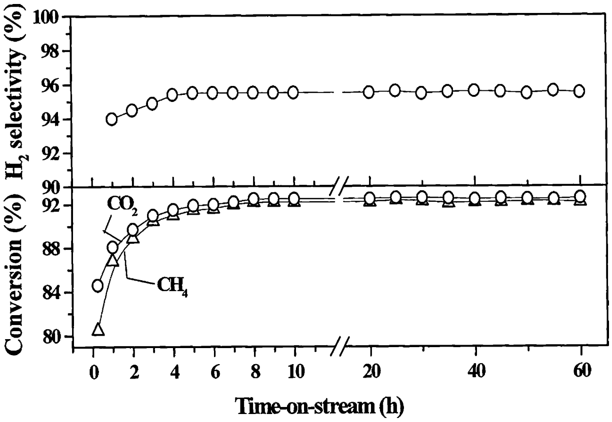

Figure 1. Time-on-steam activity and selectivity of the CoNdO$_x$ (CoNd = 1.0) catalyst in the CO$_2$ reforming of methane at 850 °C (CO$_2$/CH$_4$ mole ratio in feed = 1.1, GHSV = 20,000 cm^3/g/h).

temperature programmed reduction (TPR). Results of the catalyst characterization are presented in table 2 and figure 3.

The different crystalline phases (individual metal oxide phases and perovskite-type NdCoO$_3$ phase) present in the catalyst are strongly influenced by the Co/Nd ratio (table 2). The catalyst with Co/Nd ratio of ≥1 showed the presence of perovskite-type mixed metal oxide (NdCoO$_3$) as a major crystalline phase, with the minor (or very small) crystalline phases like Nd$_2$O$_3$, CoO, Co$_3$O$_4$ and/or Co$_2$O$_3$. The reduction of NdCoO$_3$ during the initial period of the CO$_2$ reforming process (figure 1) is expected to produce finely dispersed metallic cobalt on the Nd$_2$O$_3$ support, as in case of the reduction Ni-or Co-containing perovskite-type mixed metal oxides [20].

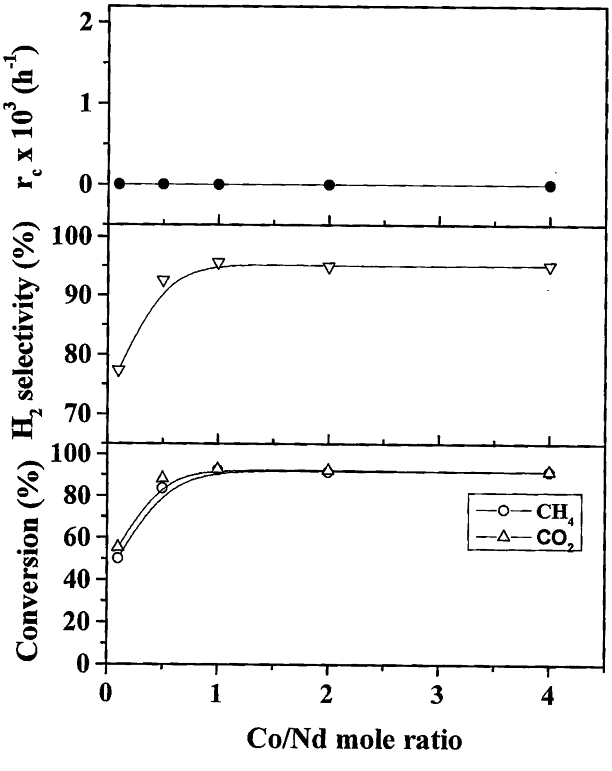

Figure 2. Influence of Co/Nd ratio on the performance (conversion, H$_2$ selectivity and rate of carbon deposition, r$_c$) of CoNdO$_x$ catalyst in the CO$_2$ reforming at 850 °C (CO$_2$/CH$_4$ = 11, GHSV 20,000 cm^3 g^{-1} h^{-1}, time-on-stream = 15 ±2 h)

The TPR of the CoNdO$_x$ catalysts (figure 3) indicates that the catalyst reduction occurs in two distinct steps, as shown by the two distinct TPR peaks. It is interesting to note that the degree of reduction in step-I is increased, and that in step-II is consequently decreased, with increasing the Co/Nd ratio (table 2). The cobalt-containing compounds present in the catalyst are reduced during the TPR, leading to the formation of metallic cobalt dispersed on Nd$_2$O$_3$, by the following stoichiometric reactions:

$$\mathrm{CoO_x + xH_2 \longrightarrow Co^\circ + xH_2O \uparrow} \qquad (1)$$

and

$$\mathrm{2NdCoO_3 + 3H_2 \longrightarrow 2CO^\circ + Nd_2O_3 + 3H_2O \uparrow} \qquad (2)$$

The above two reactions may occur in more than one steps, as follows:

$$\mathrm{Co_2O_3 \xrightarrow{H_2} Co_3O_4 + CoO \xrightarrow{H_2} Co^\circ} \qquad (3)$$

$$\mathrm{NdCoO_3 \xrightarrow{H_2} Nd_2O_3 + CoO \xrightarrow{H_2} Co^\circ + Nd_2O_3} \qquad (4)$$

A comparison of the TPR peaks for the CoNdO$_x$ catalyst reveals that, in the first step of the TPR, the cobalt in higher oxidation state [Co (III)] is reduced to lower oxidation state [Co (II)] in the first step and the reduction [Co (II) ⟶ Co°] is completed in the second step.

Results showing the temperature dependent activity and selectivity of the CoNdO$_x$ (Co/Nd = 1) catalyst are presented in Figure 4. Influence of the GHSV on the catalyst performance is presented in Figure 5. Both the H$_2$ selectivity and H$_2$/CO product mole ratio in the CO$_2$ reforming are increased with increasing the temperature or decreasing the GHSV (or increasing the contact time). These results reveal that the CO$_2$ reforming ($CH_4 + CO_2 \longrightarrow 2CO + 2H_2$) is accompanied with the reverse water–gas shift reaction (CO$_2$ hydrogenation, $CO_2 + H_2 \longrightarrow CO + H_2O$) reaction. Both the reactions are thermodynamically favoured at higher temperatures. However, over the CoNdO$_x$ catalyst, the reforming reaction is much more favoured than the CO$_2$ hydrogenation reaction at the higher temperatures and

Table 2
Surface and bulk properties and degree of reduction for the $CoNdO_x$ catalysts with different Co/Nd ratios

Co/Nd mol ratio	Surface area (m^2 g^{-1})	XRD phases	Degree of reduction (%) (temperature range)	
			Step-I	Step-II
0.1	7.3	Nd_2O_3, Co_3O_4 & Co_2O_3 (major), and $NdCoO_3^a$ (trace)	20.0 (300–460 °C)	80.0 (460–600 °C)
1.0	23.7	$NdCoO_3^a$ (major) & CoO, Co_3O_4, and Nd_2O_3 (very small)	39.6 (300–490 °C)	60.4 (490–610 °C
2.0	1.0	$NdCoO_3^a$ (major) & CoO, Co_2O_3 and Nd_2O_3	61.0 (300–530 °C)	39.0 (530–610 °C)
4.0	0.9	$NdCoO_3^a$ (major) & CoO, Co_2O_3, Co_3O_4 and Nd_2O_3	82.6 (290–510 °C)	17.4 (510–605 °C)

[a] Perovskite-type mixed metal oxide.

also at the higher contact times. The observed increase in the H_2 selectivity and H_2/CO ratio with increasing the contact time is expected because of the increase in the CO_2 conversion by the methane reforming reaction, thereby making available CO_2 at lower concentration for the CO_2 hydrogenation. It may be noted that, at all the process conditions, no carbon deposition on the catalyst in the process was observed.

The support Nd_2O_3 is basic in nature. XPS analysis of the $CoNdO_x$ with Co/Nd of 1.0 (*viz.* $NdCoO_3$) catalyst before the CO_2 reforming reaction showed two XPS peaks for O (1s) – a small peak for BE (binding energy) of 529.2 eV and a much larger peak for BE of 534.8 eV. However, after the reaction, the XPS peak at lower BE (528.9 eV) is increased very markedly, while that at higher BE shifted to lower energy (531.1 eV), indicating an increase in the basicity. The difference between the binding energies of Co ($2p_{3/2}$) and Co ($2p_{1/2}$) is 15.1 eV, which is very close to that observed for metallic cobalt. However, the binding energy for the Co ($2p_{3/2}$) is shifted towards higher binding energy side (from 777.8 to 780.2 eV). Whereas, the binding energy for Nd ($3d_{5/2}$) is shifted towards lower energy side (from 982 to 981.1 eV). These observations indicated the changes in the electronic properties of the catalyst, resulting most probably from the interaction of metallic

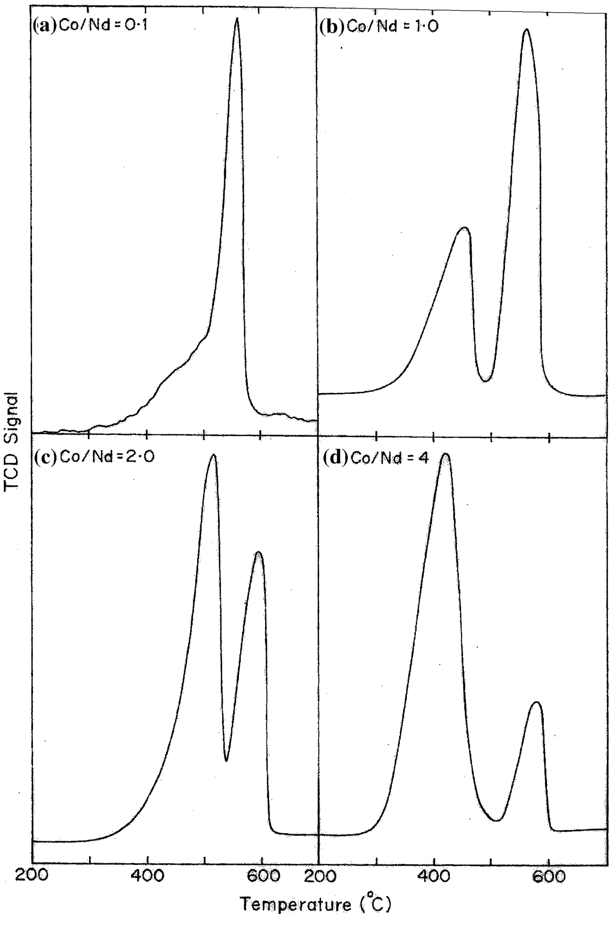

Figure 3. TPR peaks for the $CoNdO_x$ catalysts with different Co/Nd mole ratios.

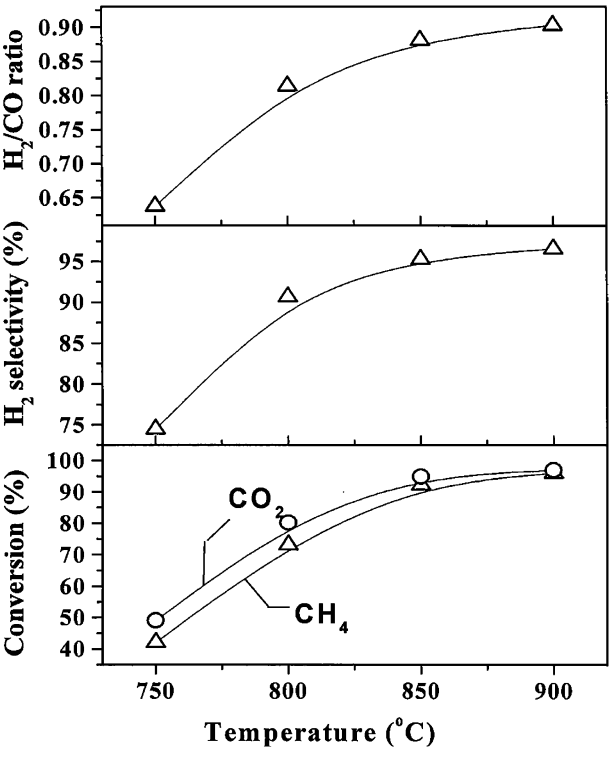

Figure 4. Performance of the $CoNdO_x$ (Co/Nd = 1.0) catalyst in the CO_2 reforming at different temperatures (CO_2/CH_4 = 1.1, GHSV = 20,000 cm^3 g^{-1} h^{-1}).

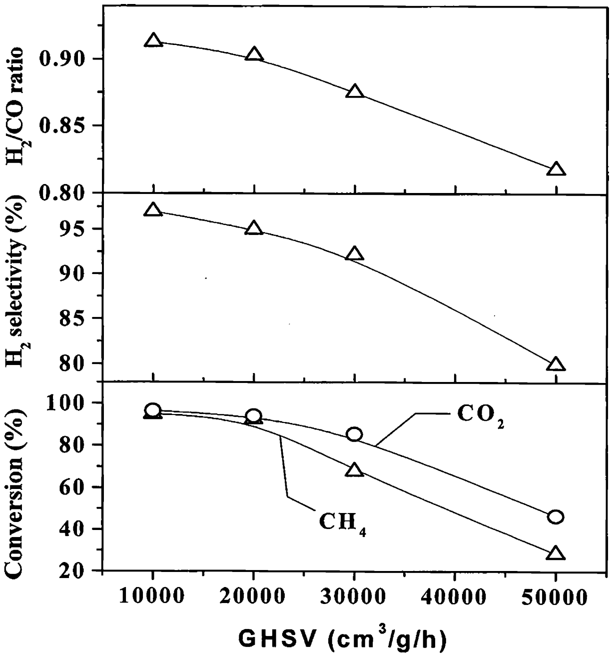

Figure 5. Performance of the CoNdO$_x$ (Co/Nd = 1.0) catalyst in the CO$_2$ reforming at different GHSVs (reaction temperature = 850 °C, CO$_2$/CH$_4$ = 1.1)

cobalt (formed during the reaction) with the support. The metallic cobalt–support (Nd$_2$O$_3$) interactions seem to be responsible for the observed inhibition to the carbon formation on the catalyst during the CO$_2$ reforming process.

Conclusions

From the studies on the dry reforming of methane over a number of Ni-, Co- and noble metal-containing catalysts and also over CoNdO$_x$ (Co/Nd = 0.1–4.0) catalysts, following important conclusions have been drawn.

(1) Among the different catalysts, the CoNdO$_x$ (Co/Nd = 1) is a highly promising catalyst for carbon-free CO$_2$ reforming of methane to syngas; the catalyst shows high activity, high selectivity and excellent stability against carbon formation during the process. No carbon formation was observed on the CoNdO$_x$ catalyst during the CO$_2$ reforming process at all the process conditions studies.

(2) For the CoNdO$_x$ catalyst, the optimum Co/Nd ratio for its best performance is found to be 1; with this ratio the catalyst is in the form of a perovskite-type mixed metal oxide (NdCoO$_3$).

(3) The CoNdO$_x$ catalyst in its active form consists of metallic cobalt dispersed on Nd$_2$O$_3$. The catalyst is reduced and converted into its active form during the initial short period of the CO$_2$ reforming process.

(4) The high resistance towards carbon formation for the CoNdO$_x$ catalyst is attributed to the strong interaction of metallic cobalt with Nd$_2$O$_3$ support, leading to an increase in the basicity of the support and/or a change in the electronic properties of the metallic cobalt finely dispersed on the support.

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