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Oxidative Conversion of Methane to Syngas over $LaNiO_3$ Perovskite with or without Simultaneous Steam and CO_2 Reforming Reactions: Influence of Partial Substitution of La and Ni

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Selective partial oxidation of methane to syngas over $LaNiO_3$, $La_{0.8}Ca$(or Sr)$_{0.2}NiO_3$ and $LaNi_{1-x}Co_xO_3$ (where $x = 0.2$–1) perovskites at extremely short contact time (≈0.8 ms) has been investigated. Also, simultaneous oxidative conversion and steam and CO_2 reforming of methane to syngas over $LaNiO_3$ at short contact time (≈9 ms) has been studied at different temperatures and CH_4/O_2 feed ratios. The catalysts, before and after reaction, were characterized by XRD and SEM. $LaNiO_3$ perovskite shows high activity and selectivity in the oxidative conversion of methane to syngas. However, the partial substitution of its La by Ca or Sr and also the partial or complete substitution of its Ni by Co causes a large decrease in both its activity and its selectivity. $LaNiO_3$ is transformed to its catalytically active form, Ni^0/La_2O_3, during the initial period of the process. This catalyst shows very good performance in the simultaneous oxidative conversion (which is exothermic) and steam and CO_2 reforming reactions (which are endothermic) of methane to syngas, at short contact time, operating in a most energy efficient manner and also requiring only a little or no external energy.

INTRODUCTION

The currently practiced steam reforming process for production of syngas from methane/natural gas is a highly energy and capital intensive process and also it provides syngas with $H_2/CO > 3$. Because of the energy crisis, efforts are being made worldwide to find a novel energy efficient (or less energy intensive) route for the production of syngas with a H_2/CO ratio of about 2.0, which is desirable for methanol and Fischer–Tropsch synthesis processes. Recently, a number of studies on catalytic partial oxidation of methane to syngas (which is exothermic and hence not at all energy intensive) with high conversion, selectivity, and desirable H_2/CO ratio, operating at extremely short (1–10 ms) (1–8), moderate (9–15), and high (16) residence times has been reported. The catalysts used in this process are as follows: NiO–CaO (1), NiO–MgO (2), NiO–rare earth oxides (3), Ni/Al_2O_3 (4, 16), supported noble metals (5–8, 11, 12), and pyrochlore and perovskite oxides containing noble metals, Ni or Co, such as Ln_2Ru_2(or Ir_2)O_7 (Ln, lanthanide) (9, 10), $LaMO_3$ (M, Ni, Rh, or Co) (13), (CaSr) (TiNi or Co)O_{3-x} (14), and $Ba_3NiRuTaO_9$ (15). Coupling of exothermic and endothermic reactions in methane-to-syngas conversion by carrying out the partial oxidation of methane simultaneously with steam reforming (17) and CO_2 reforming (18, 19) or both (20) over NiO–CaO catalyst has also been reported for eliminating hazards associated with the oxidative conversion process without losing its advantages, thus increasing the process feasibility (17, 20). Simultaneous CO_2 and steam reforming of methane over supported noble metals (21) and NiO–CaO (22) has also been investigated earlier.

Although the pyrochlore and perovskite oxide catalysts containing noble metals, viz. La_2Ru_2(or Ir_2)O_7 (9, 10) and $LaRhO_3$ (13), showed excellent performance in the oxidative conversion of methane to syngas, their use in the process is limited because of their extremely high cost. The catalytic properties of $LaNiO_3$ perovskite are expected to be altered by partial substitution for La by Sr or Ca and for Ni by Co (23, 24). It is, therefore, interesting to know the influence of the partial substitutions in $LaNiO_3$ on the catalytic activity/selectivity in the oxidative conversion of methane to syngas. The present investigation was undertaken for this purpose and also for studying the coupling of exothermic and endothermic reactions involved in the simultaneous oxidative conversion and steam and CO_2 reforming of methane to syngas over the perovskite oxide catalyst.

EXPERIMENTAL

The $LaNiO_3$, $LaNi_{1-x}Co_xO_3$, $LaCoO_3$, and $La_{0.8}Ca$ (or Sr)$_{0.2}NiO_3$ perovskite catalysts were prepared by coprecipitation method as follows. An aqueous solution containing equimolar quantities of nitrates of La (with or without Ca or Sr in requisite amounts) and Ni or Co or both (in requisite amounts) was added slowly to the aqueous

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solution of sodium carbonate under continuous stirring over a period of 1 h (the amount of sodium carbonate was 25% more than that required for the complete precipitation). The precipitate formed was kept overnight for ageing and then filtered and washed thoroughly with distilled water. It was dried in an air oven at 100°C for 15 h and then decomposed at 500°C in static air for 5 h. The decomposed mass was washed thoroughly with boiling distilled water to remove the remaining traces of Na^+, NO_3^-, and CO_3^{2-} ions and then filtered and dried at 100°C for 15 h. It was pressed binder-free to 25-mm diameter pellets, using 5 tons of pressure. The pellets are calcined in air at 900°C for 15 h and crushed to 22–30 mesh size particles (bulk density of particles, 1.8–2.0 g cm^{-3}).

The perovskite structure of all the catalysts was confirmed by XRD using a Holland Philips PW/1730 X-ray generator with the Cu $K\alpha$ radiation scintillation counter. The crystal size and morphology of the perovskite catalysts were determined by using a JSM 5200, JEOL scanning electron microscope. The surface area of the catalysts was measured by the single-point BET method by measuring the adsorption of nitrogen at liquid nitrogen temperature from a N_2–He mixture containing 30 mol% N_2, using a monosorb surface area analyzer (Quantachrome Corp., USA).

The catalytic partial oxidation of methane to syngas with or without the steam and CO_2 reforming reactions was carried out by passing continuously a gaseous feed containing pure methane (>99.95%) and oxygen (>99.9%) with or without steam and CO_2 (>99.99%) over the catalyst packed in a quartz reactor at different process conditions. The oxidative conversion reaction was carried out using 0.02 g catalyst packed in 4 mm i.d. quartz reactor, whereas the simultaneous oxidative conversion and steam and/or CO_2 reforming reactions were carried out using 0.3 g catalyst packed in 9 mm i.d. quartz reactor. In both the cases, the reactor was kept in a tubular furnace and its temperature was measured/controlled by a chromel–alumel thermocouple provided in the center of the catalyst bed. The reaction temperature could be controlled within 5°C. The gas hourly space velocity (GHSV) of the feed was measured at 0°C and 1 atm pressure. The gaseous products (after condensing the water from the product stream at 0°C) were analyzed by an on-line gas chromatography using a Spherocarb column. The C, H, and O balances across the reactor were within about 2–5% error.

RESULTS AND DISCUSSION

Catalyst Characterization

Data showing the influence of partial or complete substitution of Ni by Co and also a partial substitution of La by Ca or Sr in $LaNiO_3$ perovskite on its surface area are presented in Table 1. The substitution at both the sides results in a decrease in the surface area of the perovskite. Its surface area is decreased continuously with increasing extent of substitution of Ni by Co.

TABLE 1

Surface Area of Perovskite Oxide Catalysts and Their Specific Activity in Oxidative Conversion of Methane to Syngas at 800°C (Feed = 64.3 mol% CH_4 and 35.7 mol% O_2, GHSV = 5.2×10^5 cm^3 g^{-1} h^{-1})

		Specific activity (mmol m^{-2} s^{-1})		
Perovskite composition	Surface area (m^2 g^{-1})	CH_4 conversion	CO formation	H_2 formation
$LaNiO_3$	4.5	0.77	0.73	1.40
$LaNi_{0.8}Co_{0.2}O_3$	4.1	0.64	0.54	0.92
$LaNi_{0.6}Co_{0.4}O_3$	3.6	0.54	0.41	0.59
$LaNi_{0.4}Co_{0.6}O_3$	3.4	0.54	0.32	0.43
$LaNi_{0.2}Co_{0.8}O_3$	2.7	0.27	0.06	0.06
$LaCoO_3$	2.4	0.12	0.09	0.00
$La_{0.8}Ca_{0.2}NiO_3$	4.1	0.65	0.56	0.81
$La_{0.8}Sr_{0.2}NiO_3$	3.5	0.48	0.29	0.38

XRD spectra of $LaNi_{1-x}Co_xO_3$ oxides (where $x = 0$–1), confirming their perovskitetype structure, are shown in Fig. 1. The spectra of $LaNiO_3$ before and after the simultaneous oxidative methane conversion and steam and CO_2 reforming reactions (at 850°C, $CH_4/O_2 = 2.1$, $CH_4/CO_2 = CH_4/H_2O = 12$, GHSV = 43,100 cm^3 g^{-1} h^{-1}) are also compared in Fig. 1. The comparison reveals that, after the reaction, the perovskite ($LaNiO_3$) undergoes a drastic structural change: $LaNiO_3 \rightarrow La_2O_3 + Ni^0$. The reduction of Ni^{3+} from the pervoskite to metallic Ni is expected (23, 25) due to the syngas ($H_2 + CO$) produced in the reaction. The used catalyst shows a presence of $La(OH)_3$ phase along with Ni^0. The formation of the $La(OH)_3$ phase is due to hydrolysis of La_2O_3 by steam during the reaction and also by the exposure of the used catalyst to atmospheric moisture. In earlier studies also, Ni/La_2O_3 (26) and Ni on lanthanum modified alumina (27) showed high activity/selectivity and stability in the CO_2 reforming of methane. The initial catalytic activity of supported Ni catalysts was found to be dependent upon the metallic nickel phase (28).

Scanning electron micrograms (SEM) of the $LaNiO_3$, $LaNi_{0.4}Co_{0.6}O_3$, and $LaCoO_3$ perovskites before and after the oxidative conversion of methane to syngas (at 800°C) are presented in Fig. 2. A comparison of the catalysts before and after the reaction shows that the crystal size and morphology of the catalysts are changed after the reaction. This is expected because of the structural breakdown of the perovskites, resulting from their reduction by the H_2 and CO produced in the methane conversion reactions, followed by recrystallization of their reduction products (viz. La_2O_3 and partially and/or completely reduced Ni and Co-oxide species). After the use of the perovskites, the size of crystals for $LaCoO_3$ is larger than that for $LaNiO_3$.

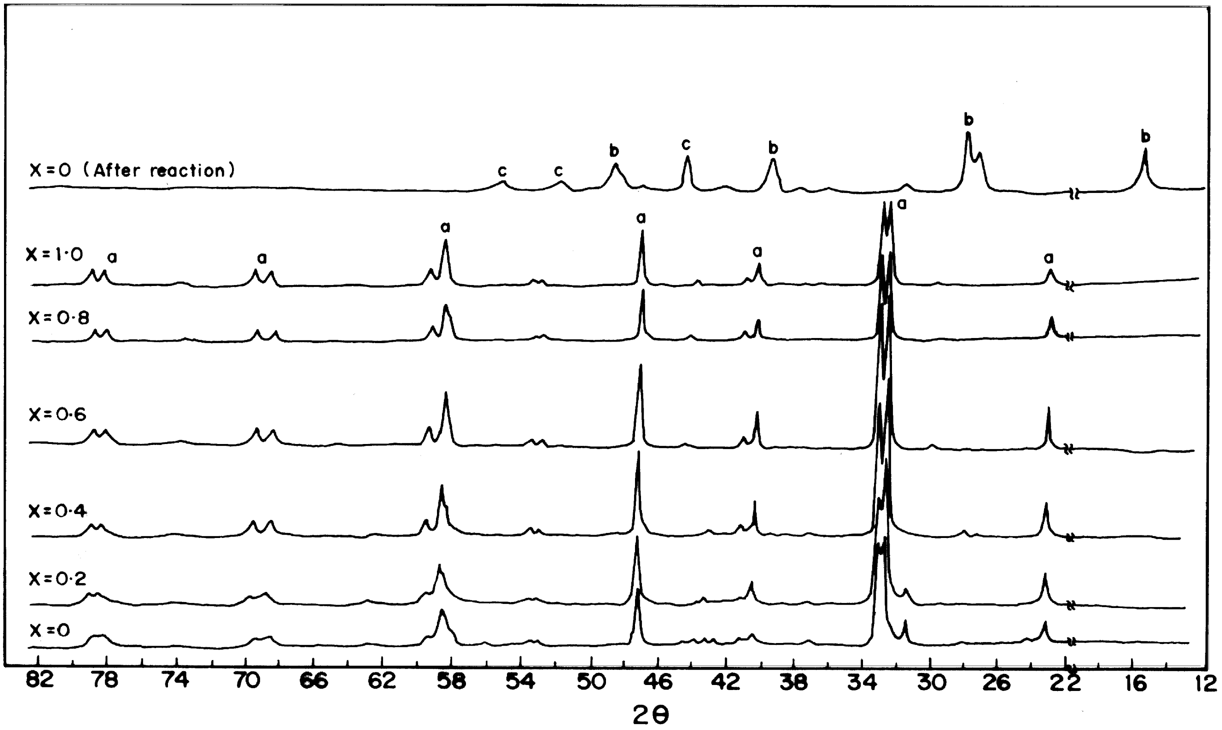

FIG. 1. XRD spectra of $LaNi_{1-x}Co_xO_3$ (where $x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) perovskite oxides before reaction and of $LaNiO_3$ after reaction (crystalline phases: (a) perovskite, (b) $La(OH)_3$, (c) Ni^0).

This coincides with the poor performance of $LaCoO_3$ (Fig. 3).

Earlier studies (29) showed that $LaCoO_3$ perovskite prepared from metal nitrate solutions contains an amorphous Co_3O_4 impurity indicated by evaluation of oxygen (150 μmol g^{-1}) between 527 and 837°C. However, in the present case, the amount of O_2 evolved from the $LaCoO_3$ is found to be much smaller (31.5 μmol g^{-1}), indicating only a very small Co_3O_4 impurity. Nevertheless, the Co_3O_4 impurity along with the perovskite is expected to be reduced (23) in the initial period of the reaction, resulting in Co/La_2O_3 or $Ni–Co/La_2O_3$.

Oxidative Conversion of Methane to Syngas

The oxidative conversion of methane to syngas over the perovskite oxide catalysts was carried out at atmospheric pressure, using a mixture of pure methane and oxygen with CH_4/O_2 mole ratio of 1.8 as a feed at a GHSV of 5.2×10^5 $cm^3\ g^{-1}\ h^{-1}$. The catalysts are compared for their specific catalytic activity in Table 1.

Figure 3 shows the influence of the partial and complete substitution of Ni by Co in $LaNiO_3$ on its activity/selectivity in the oxidative conversion of methane to syngas at 800°C and extremely small contact time ($\approx$0.8 ms). Both the conversion and the selectivity for CO and H_2 and consequently the CO space–time yield are decreased with increasing the substitution of Ni by Co. The H_2/CO product ratio is also decreased with increasing substitution, the decrease being very pronounced for the complete substitution of Ni by Co. These results reveal that, $LaNiO_3$ is highly active and selective in the reaction but $LaCoO_3$ is a much less active and not at all selective catalyst for the partial oxidation of methane to syngas. This is consistent with the fact that the latter is a good combustion catalyst (23, 24).

The selectivity (for H_2 and CO) of $LaNiO_3$ is almost same as that of the $NiO–La_2O_3$ (3), a nonperovskite catalyst, but the former is more active in the oxidative conversion of methane to syngas. This is probably because of a high dispersion and/or an uniform distribution of Ni^0 in the matrix of La_2O_3 due to the reduction of $LaNiO_3$ to Ni^0/La_2O_3 by the syngas produced during the initial period of the reaction. The reduction of $LaNiO_3$ by H_2 at different conditions has been reported earlier (23, 25, 30, 31). Earlier studies on $CaRuO_3$ (32), $LaCoO_3$ (33), and $LaNiO_3$ (34) perovskites indicated that by reduction treatment, the metal (Ru, Co, and Ni) is in a highly disperse state on a matrix composed of the respective metal oxide. In the present case also, the average crystal size of Ni^0 (31.3 nm) for $LaNiO_3$ (after use/reaction), obtained from the XRD line broadening, is found to be much smaller than that (125 nm) for $NiO–La_2O_3$ (3).

The influence of temperature on the activity/selectivity of $LaNiO_3$ in the oxidative methane-to-syngas conversion

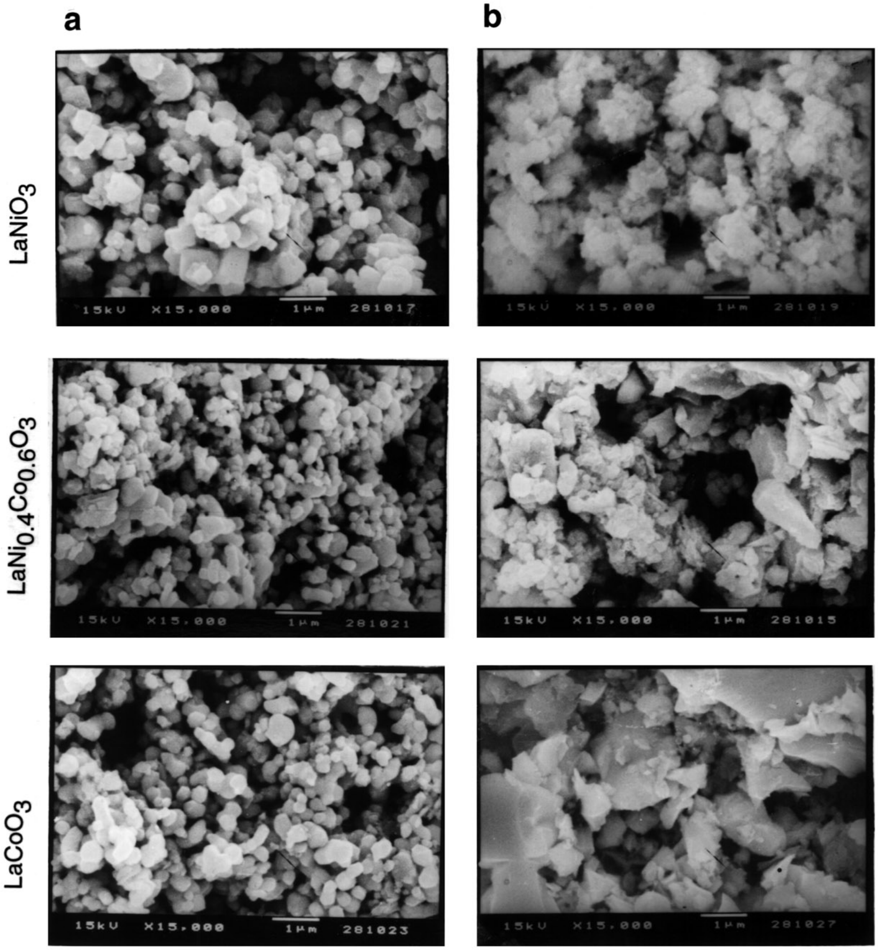

FIG. 2. SEM of $LaNiO_3$, $LaNi_{0.4}Co_{0.6}O_3$, and $LaCoO_3$ perovskite oxides (before and after the oxidative conversion of methane to syngas at 800°C).

is shown in Fig. 4. The results indicate that not only the conversion but also the selectivity for both H_2 and CO is increased with increasing reaction temperature. The increase in the selectivity is consistent with the fact that the formation of H_2 and CO in the oxidative conversion of methane is thermodynamically favored at the higher temperatures. This is because of the fact that the water gas shift reaction ($CO + H_2O \rightleftharpoons CO_2 + H_2$), which governs H_2/CO ratio, is favored at lower temperatures (below 700°C).

The time-on-stream activity/selectivity of $LaNiO_3$ in the reaction at 800°C is shown in Fig. 5. There is no significant change in both the activity and selectivity of the catalyst for a time-on-stream of 10 h.

The time-on-stream activity and selectivity data for the $La_{0.8}Ca_{0.2}NiO_3$ and $La_{0.8}Sr_{0.2}NiO_3$ catalysts are included in Fig. 5. The results reveal that both the catalysts have poor activity and selectivity as compared to that of $LaNiO_3$ and also their activity and selectivity are decreased pronouncedly with increasing the time-on-stream, indicating their fast deactivation during the catalytic process. This leads to the conclusion that the partial substitution of La by Ca or Sr in $LaNiO_3$ results in a catalyst with inferior performance in the oxidative conversion of methane to syngas.

Simultaneous Oxidative Conversion and Steam and CO_2 Reforming of Methane to Syngas

Results of the reactions of methane with O_2, CO_2, and steam, occurring simultaneously over $LaNiO_3$ perovskite, at different temperatures (at $CH_4/O_2 = 2.1$, $CH_4/H_2O = CH_4/CO_2 = 12$ and GHSV = 43,100 $cm^3\ g^{-1}\ h^{-1}$) and CH_4/O_2 feed ratios (at 850°C, $CH_4/(O_2 + 0.5CO_2 + 0.5H_2O) = 1.8$, $CO_2/H_2O = 1$, GHSV = 47,200 $cm^3\ g^{-1}\ h^{-1}$) are summarized in Figs. 6 and 7. The negative conversion of CO_2 and H_2O observed at temperatures <800°C (Fig. 6) is just indicative of the formation of CO_2 and H_2O in the process, respectively. However, when the conversion of CO_2 and H_2O is ≥ 0, the selectivity (based on methane) for CO and H_2, respectively, is 100%. The net heat of reaction (ΔH_r) for the overall process is estimated by subtracting the heat of formation (at the process temperature) of the components in the feed from that of components in the product stream.

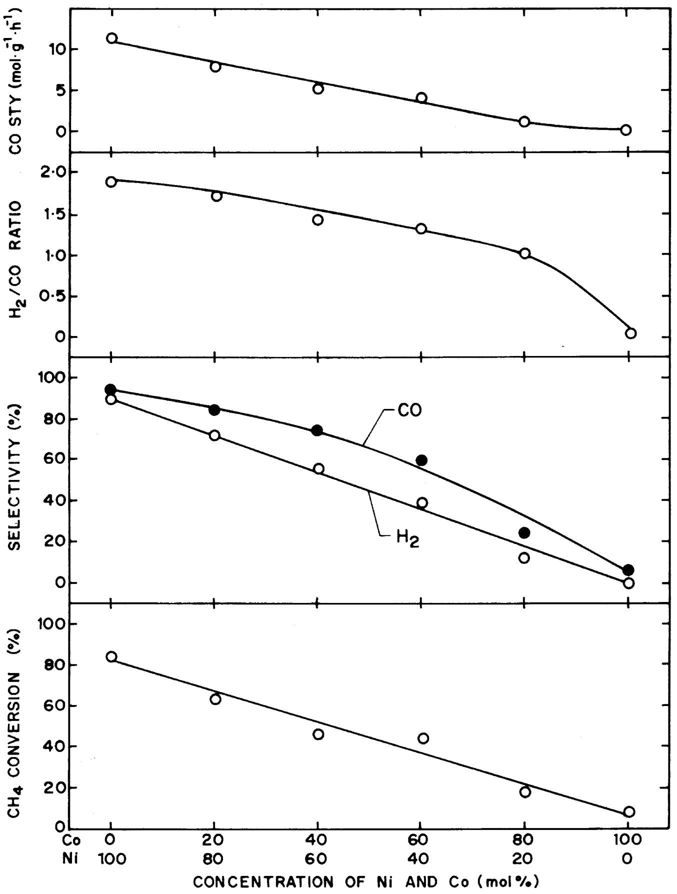

FIG. 3. Influence of relative concentration of Ni and Co in $LaNi_{1-x}Co_xO_3$ perovskite on conversion, selectivity, and space–time yield in the oxidative conversion of methane to syngas at 800°C ($CH_4/O_2 = 1.8$ and GHSV $= 5.2 \times 10^5$ $cm^3\ g^{-1}\ h^{-1}$).

In this catalytic process, following exothermic and endothermic reactions are expected to occur simultaneously.

Exothermic reactions:

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2 + 5.2\ \text{kcal mol}^{-1} \quad [1]$$

$$CH_4 + 2.0O_2 \rightarrow CO_2 + 2H_2O + 191.5\ \text{kcal mol}^{-1} \quad [2]$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 + 8.0\ \text{kcal mol}^{-1}. \quad [3]$$

Endothermic reactions:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 - 62.2\ \text{kcal mol}^{-1} \quad [4]$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 - 54.2\ \text{kcal mol}^{-1}. \quad [5]$$

Results (Figs. 6 and 7) show that high methane conversion (>90%) with almost 100% selectivity for both H_2 and CO (particularly when the conversion of H_2O and CO_2 is zero or positive) and H_2/CO product ratio of about 2.0 (which is suitable for methanol synthesis and Fischer–Tropsch processes) at very high space velocity (≈45,000 $cm^3\ g^{-1}\ h^{-1}$) could be attained in this process. Because of the coupling of

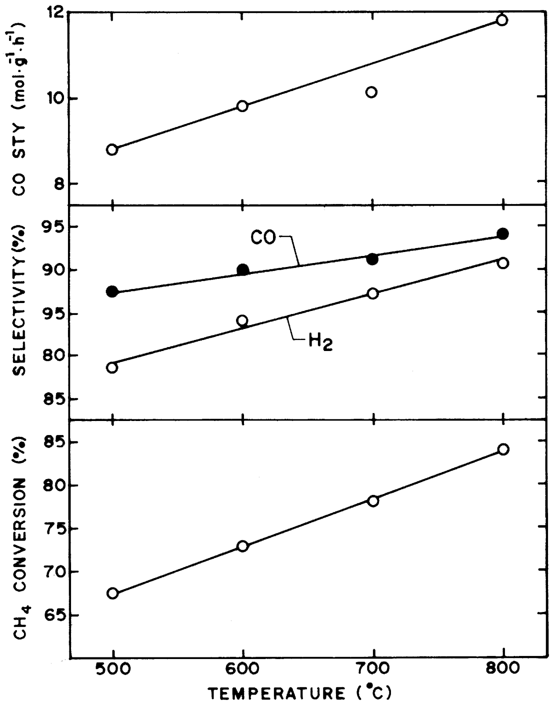

FIG. 4. Influence of temperature on conversion, selectivity, and space–time yield in the oxidative conversion of methane to syngas over $LaNiO_3$ perovskite catalyst ($CH_4/O_2 = 1.8$ and GHSV $= 5.2 \times 10^5$ $cm^3\ g^{-1}\ h^{-1}$).

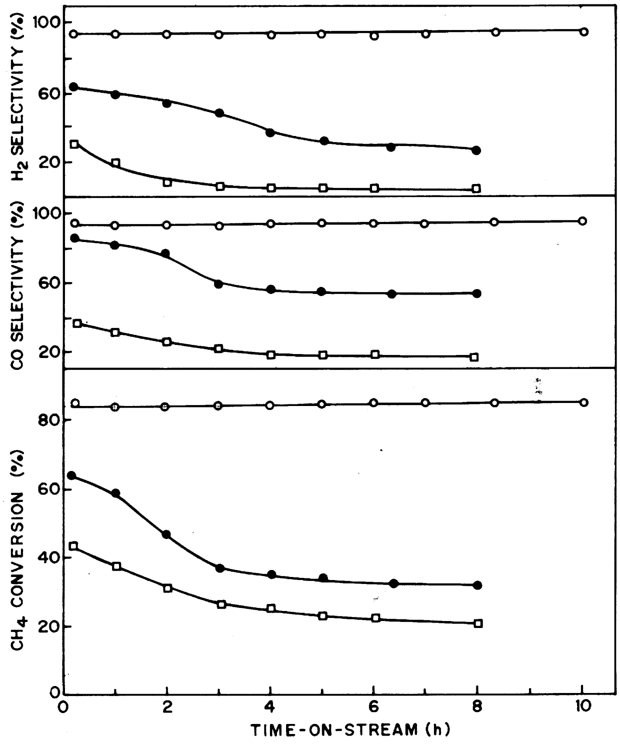

FIG. 5. Time-on-stream activity/selectivity of $LaNiO_3$ (○), $La_{0.8}Ca_{0.2}NiO_3$ (●), and $La_{0.8}Sr_{0.2}NiO_3$ (□) catalysts in oxidative conversion of methane to syngas at 800°C ($CH_4/O_2 = 1.8$ and GHSV $= 5.2 \times 10^5$ $cm^3\ g^{-1}\ h^{-1}$).

exothermic oxidation and the endothermic CO_2 and steam reforming reactions (reactions [1]–[5]) over the same catalyst, this process can be made mildly endothermic, almost thermoneutral or mildly exothermic simply by manipulating the process conditions, particularly the reaction temperature and/or CH_4/O_2 ratio in the feed. Thus, this process can occur with requiring little or no external energy. The heat produced in the process or its exothermicity is decreased markedly with increasing reaction temperature (Fig. 6) and/or CH_4/O_2 ratio in the feed (Fig. 7) due to the increase in the rate of endothermic steam and CO_2 reforming of methane (reactions [4] and [5]). Since the heat produced in the exothermic reactions (reactions [1]–[3]) is used instantly in the endothermic reactions (reactions [4] and [5]) the process is expected to occur in a most energy efficient manner and also without forming hot spots on the catalyst, consequently avoiding reaction runaway conditions.

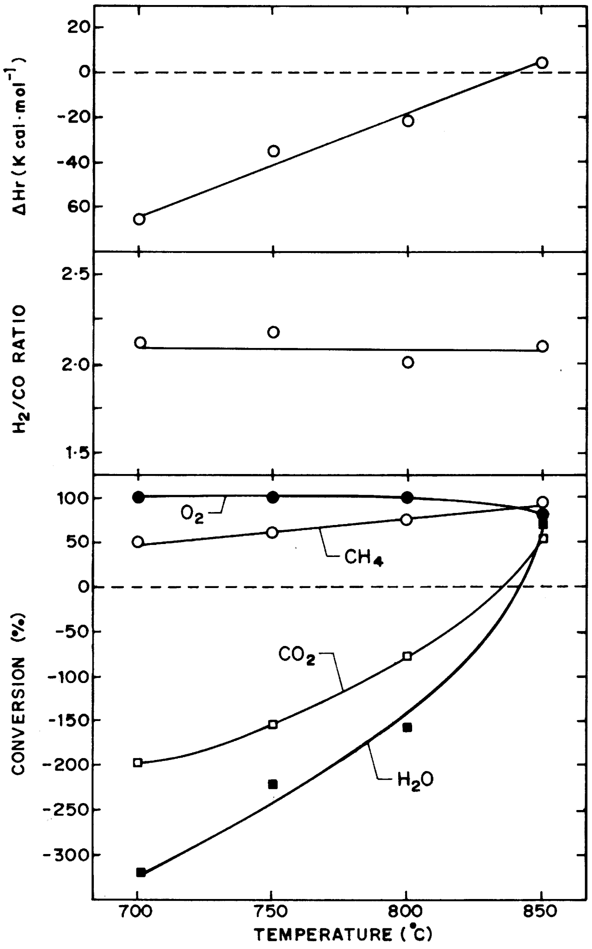

FIG. 6. Influence of temperature on conversation, H_2/CO product ratio, and net heat of reaction (ΔH_r) in the oxidative conversion of methane to syngas in presence of steam and CO_2 in the feed ($CH_4/O_2 = 2.1$, $CH_4/H_2O = CH_4/CO_2 = 12.0$, and GHSV $= 43{,}100$ cm^3 g^{-1} h^{-1}).

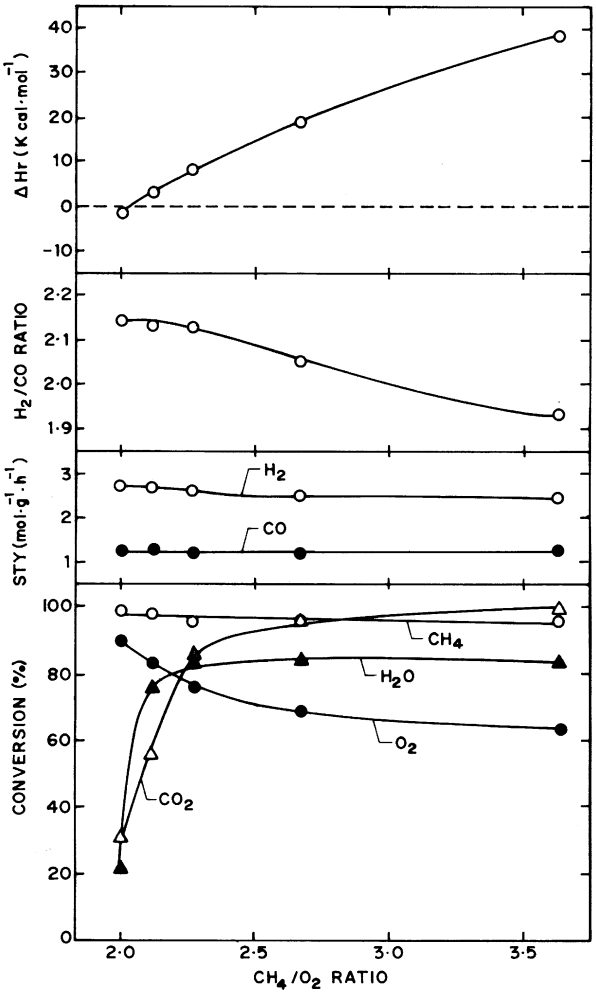

FIG. 7. Influence of CH_4/O_2 ratio in the feed on conversion, space–time yield, H_2/CO ratio, and net heat of reaction (ΔH_r) in the simultaneous oxidative conversion, steam reforming, and CO_2 reforming of methane to syngas at 850°C [$CH_4/(O_2 + 0.5CO_2 + 0.5H_2O) = 1.8$, $CO_2/H_2O = 1.0$, and GHSV $= 47{,}200$ cm^3 g^{-1} h^{-1}].

CONCLUSIONS

$LaNiO_3$ perovskite has a high potential as a catalyst for the selective partial oxidation of methane to syngas at extremely short contact time (≈0.8 ms). During the catalytic process, it is, however, transformed to Ni^0/La_2O_3, which is an active form of the catalyst during its operation in the catalytic process. However, the perovskite with partial substitution of its La by Ca or Sr or with partial or complete substitution of its Ni by Co shows inferior performance in the catalytic process. By carrying out the simultaneous oxidative conversion and steam and CO_2 reforming of methane over $LaNiO_2$ perovskite at 800–850°C and high space velocity (contact time ≈9 ms), syngas (with H_2/CO ratio of about 2.0) can be obtained with high conversion (>90%) and almost 100% selectivity (based on methane) for both H_2 and CO, while the process is operated in a most energy efficient manner, requiring little or no external energy because of the coupling of exothermic oxidative conversion and endothermic steam and CO_2 reforming reactions over the same catalyst.

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