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Partial oxidation of methane to synthesis gas over some titanates based perovskite oxides

Takashi Hayakawa [a,1], Arnfinn G. Andersen [b,1], Masao Shimizu [a],
Kunio Suzuki [a] and Katsuomi Takehira [a,1]

[a] *Oxidation Laboratory, Department of Surface Chemistry,*
National Institute of Materials and Chemical Research
(National Chemical Laboratory for Industry),
Tsukuba Research Center, AIST, 1-1 Higashi, Tsukuba, 305 Ibaraki, Japan
[b] *Section for Hydrocarbon Process Chemistry, SINTEF-SI,*
PO Box 124 Blindern, 0314 Oslo, Norway

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$Ca_{1-x}Sr_xTiO_3$-based mixed oxide catalysts containing chromium, iron, cobalt or nickel were prepared and used in the oxidation of methane. The catalyst containing cobalt or nickel showed high activity for the synthesis gas production from methane. In the case of nickel containing catalyst, nickel oxide originally separated from the perovskite structure was easily reduced to nickel metal, which showed synthesis gas production activity. In the case of the cobalt containing catalyst, pretreatment with methane was required for high activity. Reduced metallic cobalt was formed from the perovskite structure, which revealed relatively high selectivity for the oxidative coupling of methane, and afforded synthesis gas production. Both the catalysts also catalyzed carbon dioxide reforming of methane and especially both high activity and selectivity were observed over the nickel containing catalyst.

Keywords: Synthesis gas; methane oxidation; stability of perovskites; nickel metal; cobalt metal

1. Introduction

Attempts to convert methane (CH_4) directly into more valuable chemicals have focused on oxidative coupling reactions to yield ethylene and ethane [1,2] and direct oxygenation to methanol and formaldehyde [3]. Unfortunately, under conditions where reactions of CH_4 are fast enough to be of interest (>973 K), the formation of CO_2 is so favourable that partial oxidation to more useful products is difficult to achieve on an economical scale. An alternative strategy for the elaboration of CH_4 is to convert it into synthesis gas (CO and H_2), either by steam reform-

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[1] To whom correspondence should be addressed.

ing [4] or partial oxidation. This, in turn, can be converted to methanol, ammonia, alcohols, aldehydes, and higher hydrocarbons [5].

Recently, several papers have been published on the partial oxidation of CH_4 to synthesis gas. Ashcroft et al. [6] reported that transition metals, Ni, Ru, Rh, Pd, Ir, and Pt, either supported on alumina or present in mixed metal oxide precursors were active in this oxidation at temperatures of 1048 K. The partial oxidation of CH_4 to synthesis gas is also an established industrial process [7] but operates at very high temperatures (> 1473 K). Ni/Al_2O_3, a typical catalyst for steam reforming, was studied for the partial oxidation of CH_4 at temperatures > 973 K [8]. Rh/SiO_2 catalyst was also used and the activity was promoted by using rhodium vanadate as the precursor [9]. These processes were thought to involve first the oxidation of CH_4 primarily to H_2O, CO and CO_2 followed by the steam reforming reaction of CH_4 with H_2O and the water–gas shift reaction, giving fairly long reactor residence times. It is, therefore, expected that shortening of the residence times can give direct catalytic oxidation of CH_4 to synthesis gas. Platinum and rhodium surfaces in metal-coated ceramic monoliths afforded mostly H_2 and CO with almost complete conversion of CH_4 and O_2 at reaction times as short as 10^{-3} s [10]. Also, some transition metal oxides combined with alkaline earth or rare earth oxides, i.e. CoO–MgO, NiO–CaO, CoO–Yb_2O_3, or Ni/Yb_2O_3 were interestingly found to be active as the catalyst at low temperatures ($\leqslant 973$ K, down to 573 K) and extremely high space velocities in the partial oxidation of CH_4 to synthesis gas [11].

We have recently reported that some of $LaCoO_{3-\delta}$-based perovskite oxides with Ba and Fe on A- and B-sites, respectively, in the lattice are active for the oxidative coupling of CH_4 when the reaction was carried out by TPR method and cyclic operation [12]. We have also prepared and characterized a number of $CaTiO_3$-based perovskite oxides as the catalyst for partial oxidation of light hydrocarbons [13], some of which were found to be active for the oxidative dehydrogenation of ethane to ethene [14]. $CaTi_{1-y}Fe_yO_{3-\delta}$, with $0 \leqslant y \leqslant 0.4$, or $SrTi_{1-y}Fe_yO_{3-\delta}$, with $0 \leqslant y \leqslant 1.0$, were prepared and the latter containing more basic Sr metal showed higher selectivity to ethene than the former containing Ca. A few catalysts with Co on B-sites, e.g. $Ca_{0.4}Sr_{0.6}Ti_{0.4}Co_{0.6}O_{3-\delta}$, in the lattice lost their stability at 950 K, resulting in a substantial change in the product selectivity to synthesis gas formation from ethane. When these catalysts were used in the oxidative coupling of CH_4, the presence of Co or Fe substantially enhanced synthesis gas formation from CH_4 at high temperature [15]. We have studied the effects of $Ca_{1-x}Sr_xTiO_3$-based mixed oxides catalysts containing Cr, Fe, Co or Ni for the partial oxidation of CH_4 to synthesis gas.

2. Experimental

The materials used in the present study are $Ca_{1-x}Sr_xTiO_3$-based mixed oxides containing Cr, Fe, Co or Ni and were prepared by citrate process. The structure, homogeneity range and stability, as well as the details of synthesis of the materials have been reported separately [13]: Fe and Co can be substituted on Ti-sites in the lattice, while Ni and Cr cannot. The former catalysts have the general formula $Ca_{1-x}Sr_xTi_{1-y}M_yO_{3-\delta}$ with M: Fe and Co on Ti-sites in the lattice, while the latter two catalysts are below referred to as $Ca_{1-x}Sr_xTi_{1-y}Ni_y$ mixed oxide and $Ca_{1-x}Sr_xTi_{1-y}Cr_y$ mixed oxide, respectively. An important feature to be kept in mind in the following discussion, is that the surface area of the titanates without doping on B-sites was about 15 m^2/g, while the surface areas of catalysts containing M: Cr, Fe and Co were well below 5 m^2/g and that containing Ni was 8.8 m^2/g.

All materials have been tested in a mixture of air (1.0–2.5 ℓ/h) and CH_4 (0.5–1.0 ℓ/h, from Takachiko Chemical Industry Co. Ltd.) in the partial oxidation of CH_4 to synthesis gas. When we used CO_2 as an oxidant instead of air, a mixture of CH_4 (1.0 ℓ/h) and CO_2 (0.5–1.0 ℓ/h) was used. In both cases, 300 mg catalyst was dispersed in 2 ml of quartz wool to avoid sintering and clogging of the reactor. The quartz reactor used was U-shaped, with the catalyst bed near the bottom. The inner diameter of the inlet tube was 10 mm and the outlet was 4 mm. Above and below the catalyst bed the reactor was filled with quartz sand. The thermocouple was introduced from the top of the reactor, and placed in the middle of the catalyst bed. 0.5 ml of the product gases were sampled immediately after the reactor and injected into a gas chromatograph for analysis. A pretreatment of catalyst was done in a CH_4 flow (1 ℓ/h) at 1048 K for 1 h, when necessary, and thus treated catalyst was tested for the partial oxidation with air or CO_2 described above.

Before the oxidation studies, the catalysts were calcined in an air stream in the reactor for 1 h at 1048 K. The reactor was flushed with N_2 before introducing the reactants. No change in product distribution was observed after 15 min on line except over the catalyst containing Fe. All samples in the following are taken 15 min or more after establishing steady state of the reaction. Increasing temperature from 673 to 1073 K was used when the effect of temperature was studied. Finally, the whole reactor was quickly removed from the furnace with the reacting gases present, and quenched in cold water in order to preserve any phases stable only under reaction conditions.

Characterization of the catalyst was carried out as follows: the powder X-ray diffraction (XRD) diagrams were recorded by using MXP-18 (MAC Science Co.) with Cu Kα radiation. Thermal analyses (TGA/DTA) were carried out by using Shimadzu TGA 50 and DTA 50 containing electrobalance.

3. Results and discussion

The reactor filled with quartz sand and quartz wool, i.e. without catalyst, was tested with the same gas mixture as used in the catalytic reactions. The oxygen conversion stayed below 10% even at the highest reaction temperature, while the oxygen conversion was always above 90% in catalytic tests. CH_4 conversion stayed below 1% in the quartz filled reactor where the main product was ethane ($>50\%$).

3.1. OXIDATION OF CH_4 WITH AIR OVER $Ca_{1-x}Sr_xTiO_3$-BASED MIXED OXIDES

Oxidations of CH_4 with air over several $Ca_{1-x}Sr_xTiO_3$-based mixed oxide catalysts were carried out (table 1). When the fresh catalysts containing chromium, iron and cobalt were used, i.e. before CH_4 treatment, a deep oxidation mainly occurred to afford CO_2 together with small amount of synthesis gas and C_2 compounds (ethane and ethene). Iron and cobalt gave higher selectivity to the C_2 compounds compared to the other metals. Use of nickel, $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ mixed oxide, alone resulted in high activity for synthesis gas production in the fresh state. After the CH_4 treatment, activity of the catalyst containing cobalt, both $Ca_{0.8}Sr_{0.2}Ti_{0.8}Co_{0.2}O_{3-\delta}$ and $Ca_{0.6}Sr_{0.4}Ti_{0.6}Co_{0.4}O_{3-\delta}$ drastically changed to substantial production of synthesis gas together with an increase in the CH_4 conversion. Use of chromium, $Ca_{0.8}Sr_{0.2}Ti_{0.8}Cr_{0.2}$ mixed oxide, showed no change in the activity to CO_2 production even after the CH_4 treatment. $Ca_{0.6}Sr_{0.4}Ti_{0.6}Fe_{0.4}O_{3-\delta}$ afforded substantial amount of synthesis gas immediately after the CH_4 treatment, but the activity was quickly lost and the deep oxidation to CO_2 recovered in a few minutes. $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ mixed oxide alone showed high activity for synthesis gas production during the reaction, i.e., both before and after the CH_4 treatment.

3.2. STRUCTURE AND ACTIVITY OF $Ca_{1-x}Sr_xTi_{1-y}Co_yO_{3-\delta}$

Chromium cannot be substituted on Ti sites in the perovskite [13]: X-ray diffrac-

Table 1
CH_4 oxidation with air over $Ca_{1-x}Sr_xTiO_3$-based mixed oxide catalyst[a]

Catalyst	Before or after CH_4 treatment[b]	Conversion (%)		Selectivity[c] (%)			
		O_2	CH_4	CO	CO_2	H_2	C_2[d]
$Ca_{0.8}Sr_{0.2}Ti_{0.8}Cr_{0.2}$	before	94.8	19.9	1.7	94.4	0	3.8(1.1)
mixed oxide	after	94.8	20.3	1.9	94.1	2.1	3.8(1.0)
$Ca_{0.6}Sr_{0.4}Ti_{0.6}Fe_{0.4}O_{3-\delta}$	before	94.7	20.6	1.5	85.0	0	13.6(1.3)
	after	94.4	22.4	1.3	82.1	1.4	16.5(1.1)
$Ca_{0.8}Sr_{0.2}Ti_{0.8}Co_{0.2}O_{3-\delta}$	before	94.8	30.6	0.5	82.8	0	16.9(0.9)
	after	94.4	70.9	96.8	3.2	94.7	0
$Ca_{0.6}Sr_{0.4}Ti_{0.6}Co_{0.4}O_{3-\delta}$	before	94.8	23.2	0.9	82.8	1.3	5.1(0.5)
	after	94.5	69.5	98.2	1.8	97.3	0
$Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$	before	94.6	84.9	97.1	2.9	95.5	0
mixed oxide	after	94.3	85.2	97.2	2.9	96.0	0

[a] Catalyst, 300 mg; CH_4, 0.5 ℓ/h; air, 1.2 ℓ/h ($CH_4/O_2 = 2.36$); reaction temperature, 1028 K.
[b] Catalyst was treated in a CH_4 flow (1 ℓ/h) at 1048 K for 1 h.
[c] Based on CH_4.
[d] Total amount of ethane and ethene. Number in parentheses shows ethene/ethane ratio.

tion diagrams of $Ca_{0.8}Sr_{0.2}Ti_{0.8}Cr_{0.2}$ mixed oxide showed the patterns of $CaTiO_3$ (JCPDS: 42-423) having a perovskite structure and $SrCrO_4$ (JCPDS 15-356). This mixed oxide mainly catalyzed the deep oxidation together with production of small amounts of synthesis gas and C_2 compounds. It is likely that the activity for the deep oxidation is higher with $SrCrO_4$ than with $CaTiO_3$. In the case of $Ca_{1-x}Sr_xTi_{1-y}M_yO_{3-\delta}$ perovskite, iron (to $y = 1$) and cobalt (to at least $y = 0.6$) can be substituted on Ti sites [13]; $Ca_{0.6}Sr_{0.4}Ti_{0.6}Co_{0.4}O_{3-\delta}$, $Ca_{0.8}Sr_{0.2}Ti_{0.8}Co_{0.2}O_{3-\delta}$ and $Ca_{0.6}Sr_{0.4}Ti_{0.6}Fe_{0.4}O_{3-\delta}$ therefore originally have a perovskite-crystal structure and show relatively high selectivity to C_2 compounds in the fresh state. We have already mentioned an important role of the perovskite-crystal structure containing hypervalent metal ions in the oxidative coupling of methane over $LaCoO_{3-\delta}$-based mixed oxides [12]. It was also reported that synthesis gas production starts between 923 and 973 K in ethane [14] and between 973 and 1023 K in CH_4 [15] in the mixed gas flow reaction over $Ca_{0.8}Sr_{0.2}Ti_{0.8}Co_{0.2}O_{3-\delta}$ catalysts and both cases are accompanied by a phase transformation and decomposition of the catalyst at each temperature. Here also, it is most likely that a phase transformation can occur in $Ca_{1-x}Sr_xTi_{1-y}Co_yO_{3-\delta}$ catalysts during the CH_4 treatment at 1048 K.

X-ray diffraction diagrams of $Ca_{0.8}Sr_{0.2}Ti_{0.8}Co_{0.2}O_{3-\delta}$ catalysts before and after the CH_4 treatment are shown in fig. 1. In the former case, the XRD pattern of fresh $Ca_{0.8}Sr_{0.2}Ti_{0.8}Co_{0.2}O_{3-\delta}$ (a) almost coincided with that of $CaTiO_3$. The sample after the CH_4 treatment (b) showed several new peaks assigned to cobalt metal (JCPDS: 15-806) together with the peaks of $CaTiO_3$. Comparing the XRD diagrams of samples containing cobalt and nickel (fig. 1), we suggest that some cobalt is left in the bulk of the perovskite even after exposure to CH_4. It is therefore suggested that $Ca_{0.8}Sr_{0.2}Ti_{0.8}Co_{0.2}O_{3-\delta}$ can be decomposed and reduced into cobalt metal and the perovskite crystal during the CH_4 treatment. A certain line broadening of the peaks from cobalt metal can be observed, and thus we suggest an average particle size of cobalt metal below 100 nm. Fig. 2 shows the TGA (b) and DTA (c) curves observed with $Ca_{0.8}Sr_{0.2}Ti_{0.8}Co_{0.2}O_{3-\delta}$ in N_2 flow. At high temperature above 1100 K, a gradual weight loss was observed (b) together with several small peaks in DTA curve (c) although the thermal behavior of this perovskite is complex. In the measurements of the catalyst containing cobalt, the weight loss increased when the cobalt content increased. The weight loss is possibly due to the decomposition and the reduction of $Ca_{1-x}Sr_xTi_{1-y}Co_yO_{3-\delta}$ mentioned above. Nitrogen atmosphere in the thermal measurements might cause an increase in the temperature at which the phase transformation occurred because of the milder condition compared to the case of the CH_4 treatment. We observed the formation of CoO after the catalytic testing with ethane [13,14], indicating a phase separation at high temperature. In a short time of partial oxidation of ethane to synthesis gas [13], cobalt metal was not observed by X-ray diffraction, suggesting that the size of the cobalt metal particles was very small. It is likely that CoO formed from $Ca_{0.6}Sr_{0.4}Ti_{0.6}Co_{0.4}O_{3-\delta}$ and $Ca_{0.8}Sr_{0.2}Ti_{0.8}Co_{0.2}O_{3-\delta}$ by the phase separation can

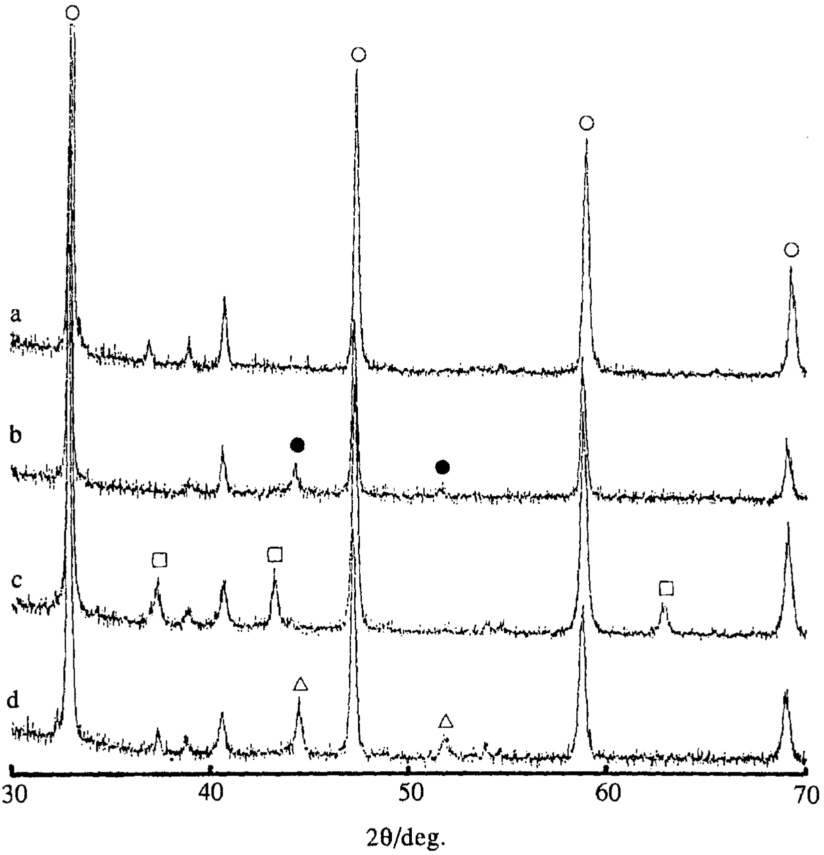

Fig. 1. X-ray diffraction diagrams of $Ca_{0.8}Sr_{0.2}Ti_{0.8}Co_{0.2}O_{3-\delta}$ and $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ mixed oxide catalyst before and after the CH_4 treatment. (a) $Ca_{0.8}Sr_{0.2}Ti_{0.8}Co_{0.2}O_{3-\delta}$; (b) $Ca_{0.8}Sr_{0.2}Ti_{0.8}Co_{0.2}O_{3-\delta}$ (reduced); (c) $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ mixed oxide; (d) $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ mixed oxide (reduced). (○) e.g. $CaTiO_3$ (e.g. JCPDS: 42-423); (●) Co metal (JCPDS: 15-806); (□) NiO (JCPDS: 4-835); (△) Ni metal (JCPDS: 4-850).

be reduced to cobalt metal of fine particles. The cobalt metal can catalyze the partial oxidation of CH_4 to synthesis gas and the particle size of the cobalt metal grow up by sintering during the synthesis gas production.

3.3. OXIDATION OF CH_4 WITH AIR OVER $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ MIXED OXIDE

$Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ mixed oxide showed high activity for synthesis gas production during the reaction, i.e., both before and after the CH_4 treatment. Nickel cannot be substituted on Ti sites in the perovskite [13], it is therefore likely that $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ mixed oxide contains nickel oxide together with the $Ca_{0.6}Sr_{0.4}TiO_3$ perovskite structure. In fact, X-ray diffraction diagrams (fig. 1) of $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ mixed oxide catalyst before the CH_4 treatment (c) clearly showed several peaks assigned to NiO (JCPDS: 4-835) which were reduced to

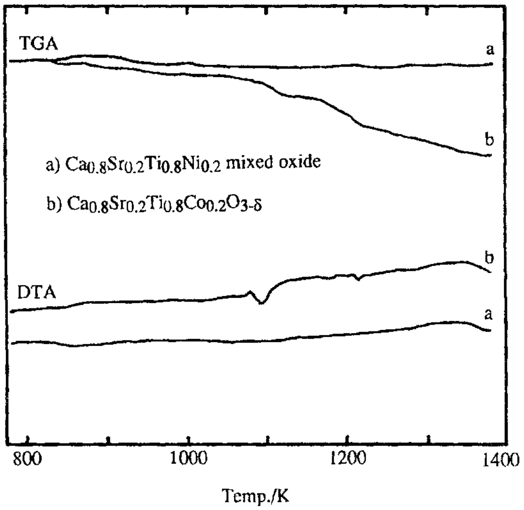

Fig. 2. TGA and DTA curves of $Ca_{0.8}Sr_{0.2}Ti_{0.8}Co_{0.2}O_{3-\delta}$ and $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ mixed oxide catalysts.

nickel metal (JCPDS: 4-850) after the CH_4 treatment (d). The predominant phase still remained as $CaTiO_3$ phase (JCPDS: 42-423). In the thermal analysis of $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ mixed oxide (fig. 2), both weight loss in TGA (a) and change in DTA curve (d) were not so clear as in the case of $Ca_{0.8}Sr_{0.2}Ti_{0.8}Co_{0.2}O_{3-\delta}$. This might be due to the small change in nickel oxide phase alone in the former case, while the latter case containing cobalt is accompanied by the phase transformation of perovskite-crystal structure itself, during the CH_4 treatment. Nickel oxide as an isolated phase can be easily reduced to nickel metal even during the oxidation reaction of CH_4. It would thus be likely that $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ mixed oxide catalyst shows high activity for the CH_4 oxidation to synthesis gas even in the fresh state. We observed an evolution of substantial amounts of hydrogen in the TPR of CH_4 over $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ mixed oxide catalyst at high temperature [12]. This fact also can be attributed to the high activity of the nickel containing catalyst for synthesis gas production from CH_4.

A temperature dependency of the reaction over $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ mixed oxide catalyst is shown in fig. 3. The CH_4 oxidation began at 650 K and the main product was CO_2 at low temperature <850 K. When the temperature went over 850 K, CO_2 production began to be lowered and was quickly replaced by the synthesis gas production. Almost complete conversion of CH_4 to synthesis gas was observed above 1000 K. These results suggest that the reaction path involves exothermic combustion of a part of CH_4 to CO_2 and H_2O with complete O_2 conversion (eq. (1)) followed by endothermic CH_4, steam and CO_2 reforming (eqs. (2) and (3)) leading to the equilibrium product distributions [6–9]:

$$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O \tag{1}$$

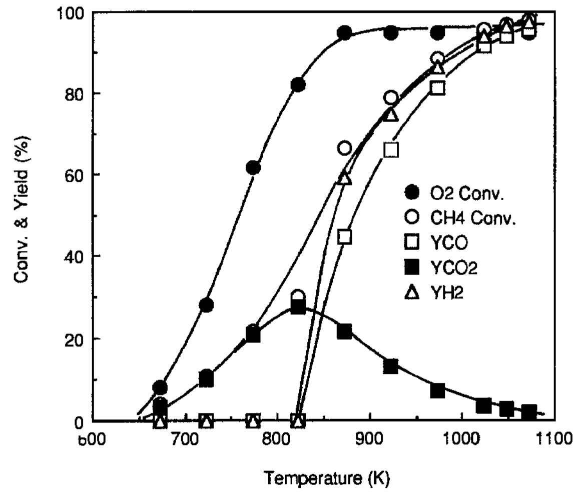

Fig. 3. Effect of temperature on the reaction results of the CH_4 oxidation with air over $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ mixed oxide catalyst.

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \tag{2}$$

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 . \tag{3}$$

3.4. OXIDATION OF CH_4 WITH CO_2 OVER $Ca_{1-x}Sr_xTiO_3$-BASED MIXED OXIDES

Nickel is well known to catalyze steam reforming of CH_4 (eq. (2)) [8]. Methane reforming with steam is used extensively in industry to form synthesis gas. The synthesis gas thus produced by steam reforming has a high H_2 to CO ratio which is suitable for processes requiring a high hydrogen content such as the synthesis gas of methanol and ammonia. In the Fischer–Tropsch reaction, on the other hand, the excess hydrogen suppresses chain growth and decreases the selectivity to the higher hydrocarbons. Carbon dioxide reforming of CH_4 produces a synthesis gas with a lower H_2 to CO ratio. Because of the high endothermicity of the reaction, it can also be used in the Solchem process where the reforming–methanation cycle can be used to transfer solar energy to chemical energy as reported by Peral [16]. Carbon dioxide reforming of CH_4 was reported to occur over a Ni/SiO_2 catalyst by Sodesawa et al. [17] and over an industrial $Ni/CaO \cdot TiO_2 \cdot Al_2O_3$ by Gadalla et al. [18].

Here, we have tried to use $Ca_{1-x}Sr_xTi_{1-y}Co_yO_{3-\delta}$ and $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ mixed oxide catalysts in carbon dioxide reforming of CH_4 (table 2). Both catalysts containing cobalt ($Ca_{0.8}Sr_{0.2}Ti_{0.8}Co_{0.2}O_{3-\delta}$ and $Ca_{0.6}Sr_{0.4}Ti_{0.6}Co_{0.4}O_{3-\delta}$) and nickel ($Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ mixed oxide) showed high activity for this reaction. When a low ratio of CH_4 to CO_2 (1.25) close to a stoichiometry (eq. (3)) was used, high yield and selectivity to synthesis gas were obtained. Fig. 4 indicates the effect of temperature on the reaction results over $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ mixed oxide catalyst. It is

Table 2
CH_4 oxidation with carbon dioxide over $Ca_{1-x}Sr_xTiO_3$-based mixed oxide catalyst[a]

Catalyst	Conversion (%)		Yield[b] (%)		Selectivity[c] (%)
	CO_2	CH_4	CO	H_2	H_2
$Ca_{0.8}Sr_{0.2}Ti_{0.8}Co_{0.2}O_{3-\delta}$[d]	31.7	27.3	31.9	15.2	47.9
$Ca_{0.6}Sr_{0.4}Ti_{0.6}Co_{0.4}O_{3-\delta}$	63.7	89.8	76.0	59.6	88.5
$Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ mixed oxide	64.6	89.6	69.0	54.8	84.8

[a] Catalyst, 300 mg; CH_4, 1.0 ℓ/h; CO_2, 0.8 ℓ/h ($CH_4/CO_2 = 1.25$); reaction temperature, 1028 K.
[b] Based on CH_4 and CO_2.
[c] Based on CH_4.
[d] Catalyst 300 mg; CH_4, 1.0 ℓ/h; CO_2, 0.6 ℓ/h ($CH_4/CO_2 = 1.67$); reaction temperature, 1028 K.

obvious that the conversions and the yields increased with the rise of the reaction temperature. The equilibrium constant for this reaction becomes greater than 1.0 when the temperature is above 909 K [17]. This catalyst containing nickel exhibited high activity for this reaction and showed near equilibrium conversion at all temperatures. Besides, the selectivity to produce synthesis gas was also considerably high and this fact was observed over the whole temperature range examined. It seems that the selectivity to synthesis gas is a significant factor for this reaction, because the reaction

$$CH_4 + CO_2 \rightleftharpoons C + CO + H_2 + H_2O \tag{4}$$

is thermodynamically possible also at high temperatures. Carbon deposition may

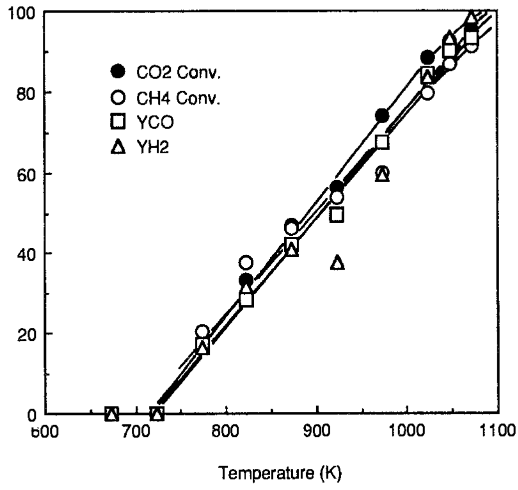

Fig. 4. Effect of temperature on the reaction results of the CO_2 reforming of CH_4 over $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ mixed oxide catalyst.

easily deactivate the catalysts. From these facts it can be said that the $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}$ mixed oxide catalyst is excellent with regard to both activity and selectivity to synthesis gas for the reaction of CH_4 and CO_2 mixtures.

4. Conclusion

$Ca_{1-x}Sr_xTiO_3$-based mixed oxide catalysts containing chromium, iron, cobalt or nickel were used in the oxidation of CH_4. It was found that the mixed oxides containing cobalt or nickel showed high activity for the synthesis gas production. In both cases, cobalt and nickel were separated from the perovskite structure, which showed relatively high selectivity for the oxidative coupling of CH_4, and showed synthesis gas production activity in the reduced metallic state. Pretreatment with CH_4 was required for high activity in the case of cobalt containing catalyst. Both the catalysts also catalyzed CO_2 reforming of CH_4 and especially both high activity and selectivity were observed over the nickel containing catalyst.

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