Selective oxidation of methane to CO and H_2 over unreduced NiO–rare earth oxide catalysts

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NiO–LnO_x (Ln = lanthanide) catalysts (with Ni : Ln = 1 : 1) without prereduction show high activity/selectivity and very high productivity in the oxidative conversion of methane to CO and H_2. The catalysts are first activated in the initial reaction, which is started at 535–560°C, by the reduction of NiO and creation of active sites. The carbon deposition on the catalysts in the reaction, particularly for the NiO–Gd_2O_3, NiO–Tb_4O_7 and NiO–Dy_2O_3 catalysts, is quite fast but it has caused a little or no influence on the catalytic activity/selectivity. Pulse reaction of pure methane on NiO–Nd_2O_3 (at 600°C) shows involvement of lattice oxygen in the initial reaction and also reveals formation of carbon from CO on the catalyst reduced in the reaction.

Keywords: Methane oxidation; NiO–rare earth oxide catalysts

1. Introduction

Catalytic partial oxidation of methane to CO and H_2 (i.e. syngas, which is a versatile feedstock for ammonia, methanol and various Fischer–Tropsch synthesis processes and also for hydrogenation and carbonylation processes),

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \quad (\Delta H = -5.4\ \text{kcal mol}^{-1})\,, \tag{1}$$

has attracted considerable interest in the last two to three years [1–11]. Unlike the methane steam reforming, it is not at all energy intensive (it is mildly exothermic) and, therefore, is of great practical importance. Recently, a few studies on the catalytic oxidative conversion of methane to syngas, operating at or close to the thermodynamic reaction equilibrium, over $Ln_2Ru_2O_7$ (where Ln = lanthanide) [1], $Ir_2Ru_2O_7$ [2], transition metal (viz. Ni, Ru, Rh, Pd, Ir and Pt) containing supported and mixed metal oxide catalysts [3], Ni/Al_2O_3 [4], and supported Ni catalysts [5]

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at temperatures above 750°C and atmospheric pressure have been reported. In these studies, high catalytic activity and selectivity was observed at temperatures above 750°C but at lower temperatures (<700°C) very poor selectivity was obtained.

Very recently, Choudhary and coworkers [6–8] have reported the oxidative conversion of methane to syngas (at atmospheric pressure) over Ni/MgO and Co/MgO [6], NiO–CaO and Ni/Al_2O_3 [7], Ni/Yb_2O_3 and CoO–rare earth oxide catalysts [8], at very high space velocities ($\geqslant 5.0 \times 10^5$ cm^3 g^{-1} h^{-1}) in a wide temperature range (300–800°C). At the higher temperatures (above 700°C), the observed methane conversion and CO selectivity values were close to the equilibrium ones. However, at the lower temperatures (below 700°C), the conversion and selectivity values were much higher than that obtained at the reaction equilibrium.

In our earlier studies, the Ni/Yb_2O_3 (i.e. reduced NiO–Yb_2O_3) catalyst showed high activity and selectivity in the oxidation of methane to syngas and the performance of the CoO–rare earth oxide catalysts was strongly influenced by the rare earth oxide present in the catalyst. It is, therefore, very interesting to know the performance of different NiO–rare earth oxide catalysts in the process. The present investigation was undertaken to study the oxidative methane-to-syngas conversion over unreduced NiO–rare earth (viz. La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er and Yb) oxide catalysts at 300–800°C at very high space velocity.

2. Experimental

The NiO–rare earth oxide (viz. La_2O_3, CeO_2, Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_4O_7, Dy_2O_3, Er_2O_3 and Yb_2O_3) catalysts (with Ni/rare earth mole ratio of 1.0) were prepared by thoroughly mixing finely ground rare earth oxide (>99.9%, Aldrich) and nickel nitrate (Loba, GR) in the required proportion with deionized water to form a thick paste, drying and decomposing in air at 600°C for 4 h and then powdering, pressing binder-free, crushing to 22–30 mesh size particles, and calcined in static air at 900°C for 6 h. The XRD analysis showed the presence of two seperate phases, NiO and rare earth oxide, in the catalysts.

The catalytic reactions were carried out at atmospheric pressure in a continuous flow microreactor (i.d. 4 mm) made up of quartz, using 20 mg catalyst placed around the tip of a chromel–alumel thermocouple. The reactor was kept in a tubular furnace. The reaction temperature was controlled by the thermocouple and the exothermic heat of reaction, particularly at lower temperature ($\leqslant$600°C), was removed by passing air through the furnace around the reactor. Before carrying out the reaction, the catalyst was heated in situ at 900°C in a flow of moisture-free N_2 (99.99%) for 1 h. The reaction water from products was condensed at 0°C. The products were analysed by an on-line gas chromatograph using Spherocarb column.

The catalytic oxidative methane-to-syngas conversion reaction over the catalysts was carried out at steady state at the following reaction conditions: feed, a mixture of pure CH_4 67 mol% and O_2 33 mol%; gas hourly space velocity (GHSV) at STP: 520 000 $cm^3\ g^{-1}\ h^{-1}$; temperature, 300–800°C. The reaction was carried out by increasing the temperature step-wise by following the temperature sequence (300 → 700°C (or 800°C) → 300°C) shown in figs. 1 and 2. The carbon deposited on the catalysts was measured by its burning at 500°C in the flow (80 $cm^3\ min^{-1}$) of O_2–N_2 mixture (5 mol% O_2) and measuring quantitatively the CO_2 and CO formed.

The pulse reaction of methane (in the absence of O_2) over the unreduced NiO–Nd_2O_3 catalyst at 600°C was carried out by injecting a number of pulses of pure methane (pulse size: 1 cm^3), one after another at an interval of about 15 min, in the quartz microreactor connected to a gas chromatograph using helium (30 $cm^3\ min^{-1}$) as a carrier gas. The details of microreactor and its operation were given earlier [12,13].

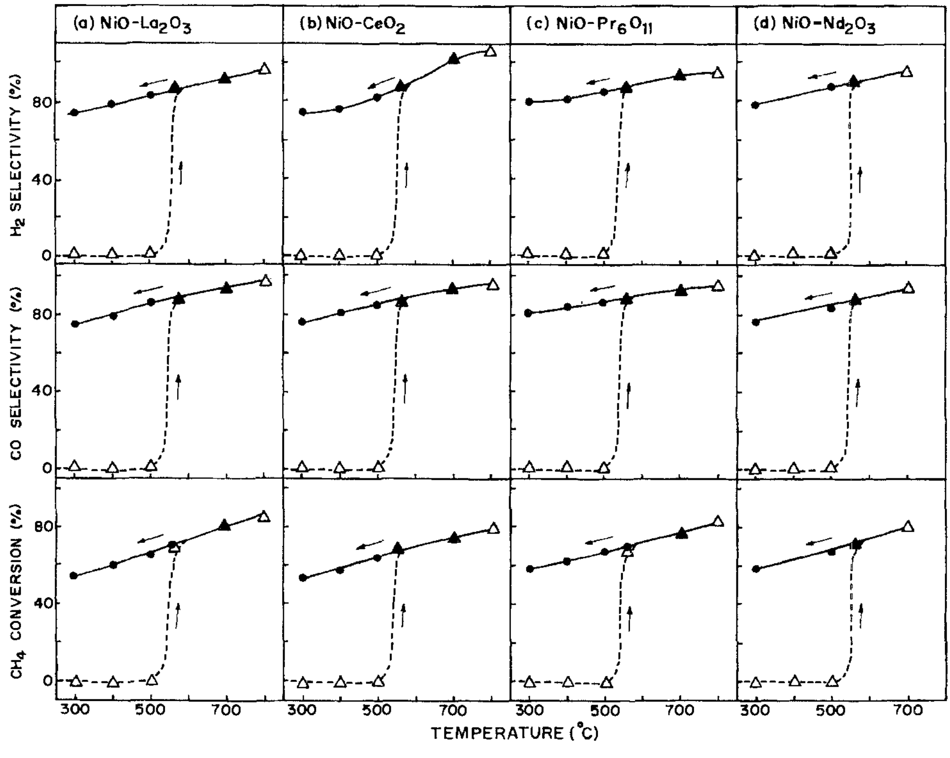

Fig. 1. Temperature dependence of the catalytic activity/selectivity of the (a) NiO–La_2O_3, (b) NiO–CeO_2, (c) NiO–Pr_6O_{11} and (d) NiO–Nd_2O_3 catalysts for the increasing temperature (△) and decreasing temperature (●) in the oxidative methane-to-syngas conversion.

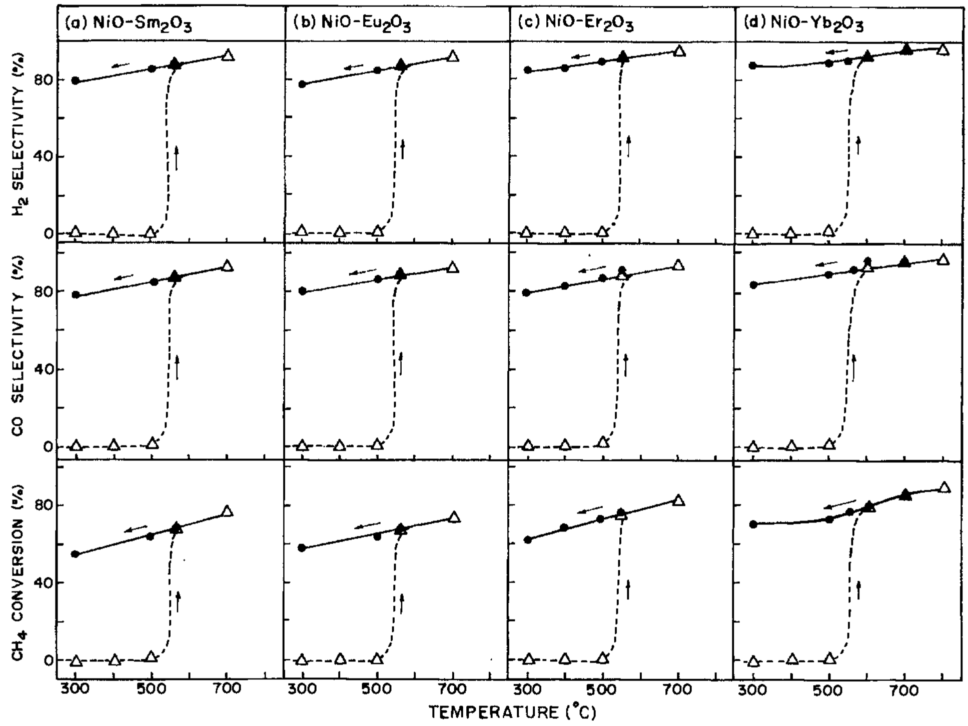

Fig. 2. Temperature dependence of the catalytic activity/selectivity of the (a) NiO–Sm_2O_3, (b) NiO–Eu_2O_3, (c) NiO–Er_2O_3 and (d) NiO–Yb_2O_3 catalysts for the increasing temperature (△) and decreasing temperature (●) in the oxidative methane-to-syngas conversion.

3. Results and discussion

The results on the oxidative conversion of methane to syngas over the NiO–rare earth (viz. La, Ce, Pr, Nd, Sm, Eu, Er and Yb) oxide catalysts (without prereduction) at different temperatures (figs. 1 and 2) reveal the following. When the temperature is increased from 300 to 700 or 800°C, the reaction occurs only at the higher temperatures. The reaction start temperature, T_s (i.e. the temperature at which the reaction on the catalyst is initiated with a sudden increase in the catalyst temperature (by a few degrees) and gas flow rate at the reactor outlet, when the temperature was increased stepwise with a temperature step of 5°C) of the catalyst is given in table 1. It is interesting to note that the reaction at low temperatures (below T_s) occurs only after carrying out the reaction on the catalysts at higher temperatures ($\geqslant T_s$) and the catalytic activity and selectivity at the higher temperatures are not changed significantly when the temperature is increased or decreased (figs. 1 and 2). The NiO in the catalysts is expected to be reduced in the initial reaction at temperature $\geqslant T_s$. When the catalysts were reduced (by H_2 at 500°C in a flow (80 $cm^3 min^{-1}$) of 20% H_2 (balance: N_2) for 1 h), the reaction start temperature was decreased by about 100°C. However, even on the reduced catalysts, the reaction

Table 1
Comparison of NiO–rare earth oxide catalysts for their reaction start temperature (T_s) and activity/selectivity in the oxidative conversion of methane to syngas at 560°C. (Feed: 67 mol% CH_4 and 33 mol% O_2; GHSV: 520 000 $cm^3\,g^{-1}\,h^{-1}$)

Catalyst	T_s (°C)	CH_4 conv. (%)	Selectivity (%)			Productivity ($mol\,g^{-1}\,h^{-1}$)	
			H_2	CO	CO_2	CO	H_2
NiO–La_2O_3	560	68.8	86.1	88.2	11.8	9.3	18.2
NiO–CeO_2	555	68.9	88.2	86.2	13.8	9.2	18.7
NiO–Pr_6O_{11}	535	68.2	86.8	88.3	11.7	9.2	18.1
NiO–Nd_2O_3	560	70.1	90.5	87.6	12.4	9.4	19.4
NiO–Sm_2O_3	560	68.2	86.1	86.6	13.4	9.1	18.1
NiO–Eu_2O_3	560	66.8	84.4	88.4	11.6	9.0	17.3
NiO–Gd_2O_3	560	71.0	89.6	86.1	13.9	9.4	19.6
NiO–Tb_4O_7	550	75.4	87.0	87.9	12.1	10.1	20.0
NiO–Dy_2O_3	550	74.3	89.8	86.9	13.1	9.9	20.5
NiO–Er_2O_3	555	75.0	90.7	88.6	11.4	10.2	20.9
NiO–Yb_2O_3	545	74.3	92.6	88.0	12.0	10.0	21.0

at lower temperatures below T_s (for reduced catalyst) is found to occur only after the catalysts had been used in the reaction at $\geqslant T_s$. These observations suggest that the active sites responsible for the low temperature catalytic activity and selectivity are arised from further reduction of the catalyst and/or formation of surface carbon species. Further investigations are necessary for understanding the above.

The results (figs. 1 and 2 and table 1) reveal that all the catalysts show high activity and selectivity (with H_2/CO ratio of about 2.0) and also extremely high productivity in the oxidative conversion of methane to syngas; the methane conversion and selectivity are increased with increasing temperature. For the activity/selectivity, the catalysts differ from each other but only to a small extent.

The activity/selectivity of the NiO–Gd_2O_3, NiO–Tb_4O_7 and NiO–Dy_2O_3 catalysts could be measured only at one temperature (560°C) because of the development of a large pressure drop across the catalyst bed due to carbon deposition on them in the reaction in a short period (tables 1 and 2).

The catalysts are compared for their reaction start temperature (T_s) and low temperature catalytic activity/selectivity (at 560°C) in table 1 and carbon deposition in table 2. It may be noted that the T_s for the NiO–rare earth oxide catalysts is between 535 and 560°C, which is much lower than that ($T_s > 750$°C) observed for the unreduced Ni–Al_2O_3 catalysts [4,14]. This matter is of practical importance because in industrial practice, catalyst prereduction by H_2, particularly for high temperature oxidation processes, is avoided. In this respect, the NiO–rare earth oxide catalysts are much superior to the Ni containing Al_2O_3 catalysts. Although

Table 2
Carbon deposition on the catalysts in the oxidative conversion of methane

Catalyst	Time-on-stream [a] (h)	Pressure drop (Δp) across catalyst bed (bar)		Carbon deposition (% wt/wt)	Average rate of coke deposition $\times 10^2$ (g (carbon) g^{-1} h^{-1})
		initial	final		
NiO–La_2O_3	6.0	0.03	0.04	9.1	1.5
NiO–CeO_2	6.2	0.03	0.12	30.4	4.9
NiO–Pr_6O_{11}	6.0	0.03	0.06	20.5	3.4
NiO–Nd_2O_3	2.8	0.03	0.20	54.6	19.5
NiO–Sm_2O_3	2.6	0.03	0.10	32.8	12.6
NiO–Eu_2O_3	2.7	0.03	0.06	16.9	6.3
NiO–Er_2O_3	4.0	0.03	0.36	56.0	14.0
NiO–Yb_2O_3	6.0	0.03	0.32	51.8	8.6
NiO–Gd_2O_3	0.6	0.03	0.35	21.2	33.7
NiO–Tb_4O_7	0.6	0.03	0.40	31.3	52.2
NiO–Dy_2O_3	0.6	0.03	0.45	28.5	47.5

[a] Total time for which the reaction carried out on the catalysts (results given in figs. 1 and 2 and table 1).

the catalysts show a small difference in their activity/selectivity and productivity, they differ widely for the carbon deposition on them in the reaction. The catalysts could be arranged for their rate of carbon deposition in the following order: NiO–Tb_4O_7 > NiO–Dy_2O_3 > NiO–Gd_2O_3 > NiO–Nd_2O_3 > NiO–Er_2O_3 > NiO–Sm_2O_3 > NiO–Yb_2O_3 > NiO–Eu_2O_3 > NiO–CeO_2 > NiO–Pr_6O_{11} > NiO–La_2O_3. The large increase in the pressure drop (table 2) is due to the carbon deposition in the interparticle space. This fact and large amount of carbon deposition (as high as about 50% wt/wt) reveal that the formation/growth of filament type carbon occurs on the catalyst. It is, however, interesting to note that there was no significant effect of the heavy carbon deposition on the activity/selectivity of the catalysts. This was confirmed by repeating the first run carried out on the catalysts (at 560°C) at the end of the experiments.

When the time-on-stream activity/selectivity of the NiO–Yb_2O_3 catalyst at 700°C was studied for a period of 6 h, there was a continuous increase in the pressure drop from 0.03 to 0.32 bar due to the carbon deposition (about 52% wt/wt) on the catalyst but no significant influence on the catalytic activity/selectivity was observed (fig. 3). This reconfirms the above observation that the catalysts are not deactivated due to the carbon deposition. Formation of coke on catalysts, which is harmless to their catalytic activity/selectivity, has also been observed earlier [15].

The carbon deposition on the catalyst is most probably due to the Boudouard reaction,

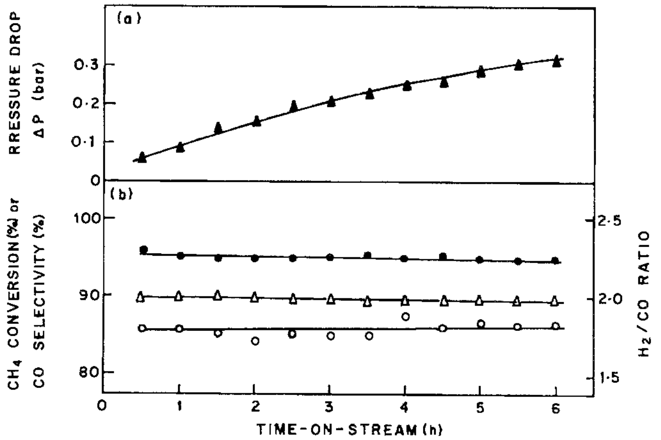

Fig. 3. Time-on-stream activity/selectivity of the NiO–Yb_2O_3 catalyst in the oxidative methane-to-syngas conversion at 700°C. (○) CH_4 conversion, (●) CO selectivity, (△) H_2/CO product mol ratio, and (▲) pressure drop, Δp across the catalyst bed.

$$2CO \rightarrow C + CO_2\,, \tag{2}$$

and the heterogeneous water–gas reaction,

$$CO + H_2 \rightarrow C + H_2O\,, \tag{3}$$

occurring simultaneously in the oxidative methane conversion process. When a pulse reaction of pure methane (in the absence of free O_2) on the used (i.e. activated in the oxidative methane conversion reaction at 700°C for 1 h) NiO–Nd_2O_3 and NiO–Yb_2O_3 was carried out at 600 and 700°C, respectively, the methane conversion was found to be 0.2 and 0.5%, respectively. However, in the pulse reaction over the unreduced NiO–Nd_2O_3 at 600°C in the absence of free O_2, the methane conversion and yield of CO and surface carbon were quite appreciable depending upon the pulse number (table 3). These observations clearly show that the carbon deposition on the catalyst is not due to a methane decomposition reaction,

$$CH_4 \rightarrow C + 2H_2\,, \tag{4}$$

and the formation of surface carbon requires the presence or formation of CO so that the reactions (2) and (3) can occur.

The formation of CO and CO_2 in the pulse reaction of pure methane (in the absence of free O_2) over the unreduced NiO–Nd_2O_3 at 600°C (table 3) indicates an involvement of lattice oxygen from the catalyst, particularly from the reducible NiO, in the reaction. In the pulse reaction, the total conversion of methane and the yield and selectivity for CO and CO_2 passed through a maximum, whereas the yield for carbon deposition is increased continuously with increasing the pulse number. These observations reveal that the catalyst reduction (i.e. reduction of NiO) is involved in the activation of unreduced catalyst and the degree of catalyst reduction plays an important role in deciding the methane conversion activity and

Table 3

Results of pulse reaction of methane (in absence of free O_2) on NiO–Nd_2O_3 (unreduced) catalyst at 600°C. (Pulse reaction condition: amount of catalyst, 20 mg; carrier gas (He) flow, 30 $cm^3\ min^{-1}$; pulse size, 1.0 cm^3 and pressure, 1.8 atm)

Pulse No.	CH_4 conv. [a] (%)	Yield [b] (%)			Selectivity [c] (%)	
		CO	CO_2	carbon on catalyst	CO	CO_2
1	1.2	0.03	0.8	0.37	2.0	63.3
2	6.5	0.9	5.0	0.6	13.4	78.1
3	26.2	6.5	16.9	2.8	24.8	64.5
4	21.8	10.6	8.0	3.2	50.0	36.7
5	18.5	11.7	2.0	4.8	63.2	10.8
6	15.5	8.4	1.0	6.1	54.2	6.5

[a] Total conversion of methane based on the methane balance in the reactor inlet and outlet pulse.

[b] Methane conversion (%) to a particular product.

[c] Product selectivity (%) = [yield (%) / total conversion (%)]×100.

also the selectivity for the formation of CO, CO_2 and surface carbon. The formation of surface carbon is favored on the more and more reduced catalyst. On the oxidized catalyst the formation of CO_2 over CO is favored, the CO/CO_2 ratio is increased with increasing the pulse number and consequently with the degree of catalyst reduction. The increase in the methane conversion with increasing pulse number suggests that the catalytic activity is increased with increasing the degree of catalyst reduction. The decrease in the conversion above the pulse number 4 is due to the depletion of lattice oxygen and/or decrease in the diffusion rate of the lattice oxygen from bulk to surface of the NiO (in the catalyst), with further increase in the pulse number.

4. Summary

We report here our preliminary studies disclosing the use of unreduced NiO–rare earth oxide catalysts in the oxidative conversion of methane to syngas (H_2/CO = 2.0) with high conversion, selectivity and productivity at 300–800°C and extremely high space velocity. In the process, the unreduced catalysts are first activated in the initial reaction, which is started at 535–560°C depending upon the catalyst, by the reduction of NiO and creation of active sites and then could be used for the process at temperatures below the reaction start temperature. In the process, the carbon deposition on the catalysts, particularly on the NiO–Gd_2O_3, NiO–Tb_4O_7 and NiO–Dy_2O_3, is, however, quite fast. The carbon on the catalyst is harmless for their catalytic activity/selectivity but causes a large increase in the pressure drop across the catalyst bed due to blockage of void volume or space between the catalyst particles by the carbon. The pulse reaction of pure methane (in the absence of free O_2) over the unreduced and used (or active) NiO–Yb_2O_3 catalysts revealed the involvement of lattice oxygen in the initial reaction, the formation of carbon from CO on the catalyst reduced in the reaction and also importance of degree of catalyst reduction in deciding the catalytic activity and product (including carbon) selectivity.

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