

# NiO-Alkaline Earth Oxide Catalysts for Oxidative Methane-to-Syngas Conversion: Influence of Alkaline Earth Oxide on the Surface Properties and Temperature-Programmed Reduction/Reaction by H<sub>2</sub> and Methane

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Temperature-programmed reaction of pure methane from 100–900°C with NiO-MgO, NiO-CaO, NiO-SrO, and NiO-mixed alkaline earth oxides (viz., MgO-CaO, MgO-SrO, MgO-BaO, CaO-SrO, CaO-BaO, and SrO-BaO) with Ni/alkaline earth element(s) ratio of 1.0 (calcined at 930°C for 4 h) has been studied. Temperature-programmed reduction of these catalysts and NiO-MgO with different Ni/Mg ratios by H<sub>2</sub> from 100°C to 900°C has also been thoroughly investigated. The NiO-CaO, NiO-MgO-CaO, and NiO-MgO catalysts show increasingly superior performance in the oxidative conversion of methane to CO and H<sub>2</sub> at a very low contact time (1 ms). However, the presence of higher alkaline earth oxide (SrO and/or BaO) causes a large decrease or almost complete deactivation of the NiO-containing alkaline earth oxide(s) catalyst for the reaction. The catalysts before and after reduction (by H<sub>2</sub> at 500°C) are characterized for their relative surface composition of Ni and alkaline earth element(s) by XPS. Because of the reduction, the surface Ni/alkaline earth(s) ratio for all the catalysts is decreased; the decrease is, however, very large for the NiO-SrO and all the BaO containing catalysts. © 1998 Academic Press

catalysts is reduced to its metallic form (Ni<sup>0</sup>) in the initial short period of the methane-to-syngas conversion reactions (1,6). The oxidative methane-to-syngas conversion with or without simultaneous steam and/or CO<sub>2</sub> reforming reactions over NiO-alkaline earth oxides is a promising process of great practical importance. Hence, it is of both scientific and technological interest to compare different NiO-alkaline earth oxide or mixed alkaline earth oxide catalysts for this process and also for their reaction with pure methane, reduction by H<sub>2</sub>, and surface properties.

The present investigation was undertaken with the objective of comparing the different NiO alkaline earth oxide and mixed alkaline earth oxide catalysts (calcined at 930°C) for their (i) temperature programmed reaction with pure methane (in the absence of free O<sub>2</sub>) from 100° to 900°C, (ii) temperature programmed reduction by H<sub>2</sub> from 100° to 900°C, (iii) catalytic activity/selectivity in the oxidative conversion of methane to syngas at a very low contact time, and also (iv) surface properties (viz. surface area and relative surface composition of Ni and rare earth elements).

## INTRODUCTION

NiO-MgO (1–5) and NiO-CaO (2, 6–10) catalysts show high activity/selectivity in the methane-to-syngas (CO and H<sub>2</sub>) conversion reaction involving partial oxidation of methane (1–3), steam reforming and/or CO<sub>2</sub> reforming of methane (4,5,7) or in all these reactions occurring simultaneously over the catalyst (4, 8–10). However, our preliminary studies revealed that the presence of higher alkaline earth oxide(s) (SrO and BaO) in the nickel containing alkaline earth oxide(s) catalysts causes a drastic reduction in their activity and selectivity for the above reactions. NiO forms a complete solid solution with MgO at higher calcination temperatures (11–13) but not with the higher alkaline earth oxides. The NiO from NiO-MgO and NiO-CaO

## EXPERIMENTAL

The NiO-alkaline earth oxide(s) catalysts (Table 1) with Ni/alkaline earth(s) mole ratio of 1.0 were prepared by mixing thoroughly finely ground high purity nickel nitrate and required alkaline earth hydroxide(s) (with required mole ratio(s)), along with deionized water just sufficient to form a thick paste, drying and decomposing the mass at 600°C for 4 h, powdering, pressing, and crushing to 30–60 mesh particles and calcining in air at 930°C for 4 h. The catalysts after calcination are stored in a desiccator over NaOH pellets. In the Ni-containing mixed alkaline earth oxides, the concentration of alkaline earth oxides was equimolar.

The catalysts were characterized for their surface area by single point BET method using a Surface Area Analyzer (Quantachrome, USA). The catalysts, before and after their reduction (by H<sub>2</sub> at 500°C for 1 h) and passivation (by O<sub>2</sub>

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**TABLE 1**  
**Results of the Oxidative Conversion of Methane to Syngas (at 700°C) over Ni-Containing Alkaline Earth Oxide Catalysts Reduced at 500°C and 900°C**

Catalyst	CH <sub>4</sub> conversion (%)	Selectivity (%)			H <sub>2</sub> /CO mole ratio	CO productivity (mol · g <sup>-1</sup> · h <sup>-1</sup> )
		H <sub>2</sub>	CO	CO <sub>2</sub>		
<i>Catalyst reduced at 500°C</i>						
NiO-MgO	86.8	95.2	95.3	4.7	2.0	12.4
NiO-CaO	80.0	86.8	87.0	13.0	2.0	10.4
NiO-SrO	0.44	--	--	100.0	--	--
NiO-MgO-CaO	85.1	90.2	92.4	7.6	2.0	12.0
NiO-CaO-SrO	40.0	55.5	72.6	27.5	1.5	4.4
NiO-MgO-SrO	45.9	58.7	76.1	23.9	1.5	5.2
NiO-MgO-BaO	No reaction					
NiO-CaO-BaO	No reaction					
NiO-SrO-BaO	No reaction					
<i>Catalyst reduced at 900°C</i>						
NiO-MgO	86.6	95.1	95.4	4.6	2.0	12.3
NiO-SrO	23.4	55.8	31.8	68.2	3.2	1.1
NiO-MgO-SrO	53.0	64.4	77.0	23.0	1.6	6.1
NiO-CaO-SrO	33.9	56.7	48.8	51.2	2.3	2.4
NiO-MgO-BaO	1.5	0.0	0.0	100.0	—	—
NiO-CaO-BaO	No reaction					
NiO-SrO-BaO	No reaction					

at low concentration (1 mol% in N<sub>2</sub>) at room temperature for 1 h), were characterized for their surface composition of nickel and rare earth elements by XPS using a VG - Scientific ESCA -3 MK II electron spectrometer C 1s (with binding energy = 285 eV) was used as an internal standard, and also for their Ni<sup>0</sup> and NiO phases by powder XRD (using a Holland Philips, PW/1730 X-ray generator with CuK $\alpha$  radiation and scintillation counter) while taking maximum care to avoid exposure of the catalysts to atmospheric moisture and CO<sub>2</sub>.

The temperature-programmed reaction of methane (in the absence of free-oxygen) over the unreduced catalysts was carried out in a quartz reactor (ID = 10 mm) by passing a mixture of methane and helium (5 mol% CH<sub>4</sub>) at a flow rate of 100 cm<sup>3</sup> min<sup>-1</sup> over 0.3 g unreduced catalyst from 100 to 900°C at a linear heating rate of 20°C min<sup>-1</sup>. The reaction products were sampled at different temperatures, using a 16-loop gas sampling valve and analyzed by GC using a Spherocarb column. The temperature-programmed reduction (TPR) of the unreduced catalysts was carried out in a quartz reactor (ID = 4.5 mm), packed with 0.05 g catalyst in a flow (60 cm<sup>3</sup> min<sup>-1</sup>) of a H<sub>2</sub>-Ar mixture (2.0 mol% H<sub>2</sub>) from 100–900°C at a linear heating rate of 10°C min<sup>-1</sup>. The hydrogen consumed in the TPR was measured quantitatively by TCD. Before carrying out the temperature-programmed reaction with methane or reduction by H<sub>2</sub>, the catalyst was pretreated *in situ* at 900°C for 1 h in a flow of moisture-free helium (50 cm<sup>3</sup> min<sup>-1</sup>).

The partial oxidation of methane to syngas over the catalysts was studied at 700°C and atmospheric pressure by

passing a gaseous mixture of pure methane (99.95%) and oxygen with CH<sub>4</sub>/O<sub>2</sub> mole ratio of 1.8 at a space velocity (measured at 0°C and 1 atm) of 5.1 × 10<sup>5</sup> cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup> (contact time = 1 ms) over the catalyst (0.02 g) packed in a quartz reactor (ID = 4 mm); the reactor was kept in a tubular furnace (ID = 25 mm). The reaction temperature was measured/controlled by a chromel–alumel thermocouple provided in the centre of the catalyst bed. The reaction temperature could be controlled within 5°C. The reaction product (after condensing water from the product stream at 0°C) was analyzed by an on-line gas chromatograph using a Spherocarb column. Before the reaction, the catalyst was reduced *in situ* in a flow (50 cm<sup>3</sup> min<sup>-1</sup>) of H<sub>2</sub>-N<sub>2</sub> mixture (30 mol% H<sub>2</sub>) at 500°C or 900°C for 1 h.

## RESULTS

### *Oxidative Conversion of Methane to Syngas*

Results showing the influence of alkaline earth oxide(s) on the conversion of methane and selectivity for CO and H<sub>2</sub> of the NiO-alkaline earth oxide(s) catalysts (reduced before the reaction by H<sub>2</sub> at 500°C and also at 900°C) in the oxidative conversion of methane to syngas (at 700°C) are presented in Table 1. Among the catalysts, the NiO-MgO, NiO-CaO, NiO-MgO-CaO show high methane conversion and also high selectivity for both H<sub>2</sub> and CO in the reaction. The NiO-MgO and NiO-MgO-CaO catalysts showed no sign of deactivation when tested continuously for 30 h. However, both the activity and selectivity of the NiO-MgO and NiO-CaO catalysts is drastically reduced and almost

vanished when SrO and BaO, respectively, are added to either of the former catalysts. The NiO-SrO catalyst shows a poor activity/selectivity for the reaction, but it is deactivated completely when BaO is added to the catalyst.

The activity and selectivity of the NiO-SrO and NiO-MgO-SrO catalysts are increased appreciably with increasing their reduction temperature from 500°C to 900°C. On the contrary, an opposite effect is observed for the NiO-CaO-SrO catalyst. The BaO containing catalysts, however, remained inactive even after increasing the reduction temperature from 500°C to 900°C.

#### Temperature Programmed Reaction of Methane in the Absence of Free-O<sub>2</sub>

Results of the temperature programmed reaction of methane in absence of free -O<sub>2</sub> over the unreduced catalysts from 100°C to 900°C are presented in Figs. 1–3. It is interesting to note that the trends for the conversion of methane (by its reaction with the lattice oxygen of NiO producing CO, CO<sub>2</sub>, H<sub>2</sub>O and/or its dissociation on Ni<sup>o</sup> produced in the gas solid reaction)—to total and to CO, CO<sub>2</sub>, and adsorbed carbon species, vary from catalyst to catalyst. From the results (Figs. 1–3), the following important observations could be made:

(1) The gas solid reaction between NiO and methane or the reduction of NiO by methane for NiO-MgO and NiO-CaO catalysts is initiated at about 600°C but for the SrO and/or BaO-containing catalysts it is at higher temperatures.

(2) The methane conversion reaction over the CaO catalyst is much faster at lower temperatures. However, the ad-

dition to this catalyst of SrO or BaO results in a decrease in the methane conversion and also causes a shift in the methane conversion maximum towards the higher temperature side (from 700°C to 850°C).

(3) For all the catalysts except NiO-CaO, high methane conversion is observed only at the higher temperatures (above 800°C).

(4) The formation of CO<sub>2</sub> in the reaction is observed only for the NiO-CaO, NiO-SrO, and NiO-CaO-SrO catalysts and that of CO is observed for all the catalysts, except for the NiO-MgO-BaO and NiO-SrO-BaO. However, the formation of adsorbed carbon species are observed for all the catalysts to an appreciable extent. For the NiO-MgO-BaO and NiO-SrO-BaO, the methane is converted almost completely to the adsorbed carbon species; in these cases, no CO or CO<sub>2</sub> is detected in the product stream.

#### Temperature Programmed Reduction by H<sub>2</sub>

Curves for the temperature-programmed reduction (TPR) by H<sub>2</sub> of the NiO-MgO (with different Ni/Mg ratios), NiO-CaO, NiO-SrO, and NiO-containing mixed alkaline earth oxides from 100° to 900°C are presented in Figs. 4–6. The data on the TPR peak maximum temperatures of the catalysts along with their surface area are provided in Table 2. The following observations have been made from the TPR studies:

(1) In the case of NiO-MgO catalysts (Ni/Mg = 0.1–10), the TPR start temperature is decreased and the hump of the TPR curve at about 550°C is increased with increasing the temperature (Fig.4). The TPR peak maximum temperature

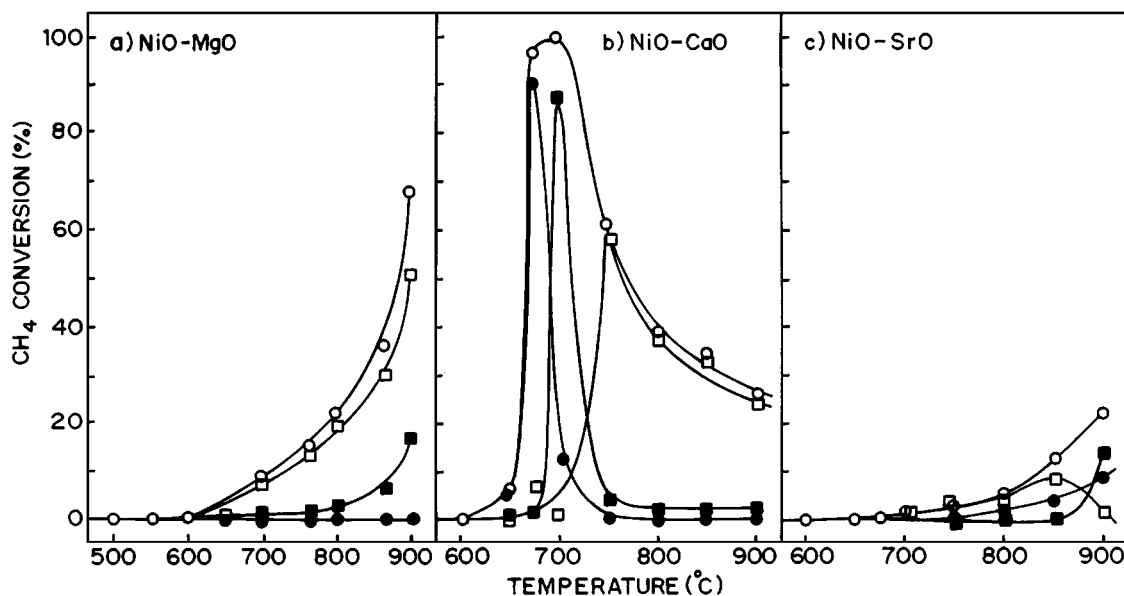


FIG. 1. Temperature-programmed reaction of methane with NiO-MgO, NiO-CaO, and NiO-SrO catalysts in the absence of free-O<sub>2</sub> (conversion of methane—total (○), to CO<sub>2</sub> (●), to CO (■), and to adsorbed carbon species (□)).

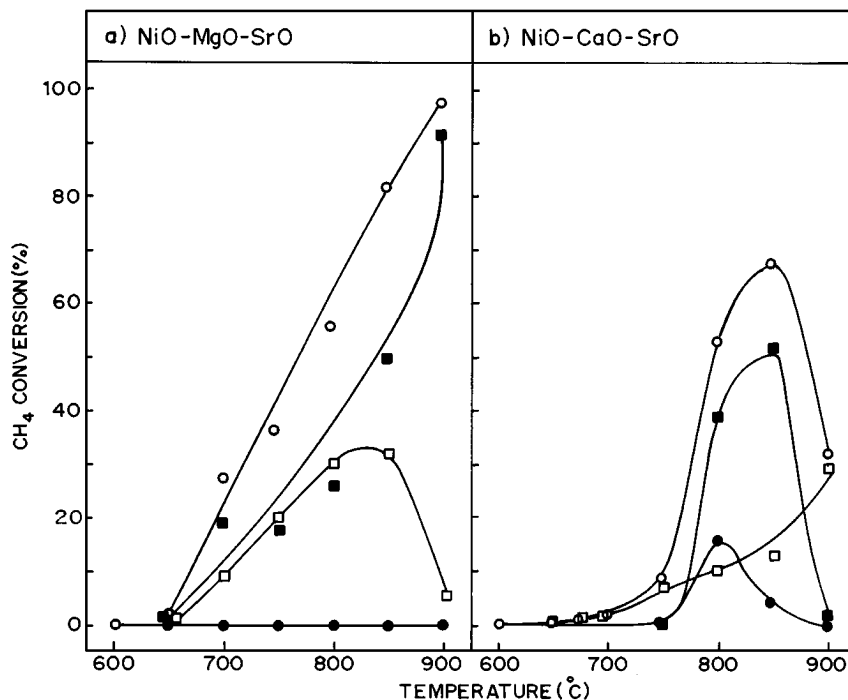


FIG. 2. Temperature-programmed reaction of methane with NiO-MgO-SrO and NiO-CaO-SrO catalysts in the absence of free-O<sub>2</sub> (conversion of methane—total (○), to CO<sub>2</sub> (●), to CO (■), and to adsorbed carbon species (□)).

for the catalyst with Ni/Mg = 0.1–10.0 is appreciably lower (805°C) than that (>900°C) for the other catalysts with Ni/Mg ≤ 3.0.

(2) Among the NiO-alkaline earth metal oxide(s) (Ni/alkaline earth(s) = 1.0) catalysts, the TPR of the NiO-MgO and NiO-CaO catalysts has a single peak at ≥900°C

and 490°C, respectively. Whereas, for the other catalysts, their TPR has a two-peak maxima, as shown in Figs. 5 and 6, indicating the presence of NiO in the two different environments.

(3) For all the catalysts containing MgO, the TPR peak maximum temperature is, in general, much higher (≥850°C)

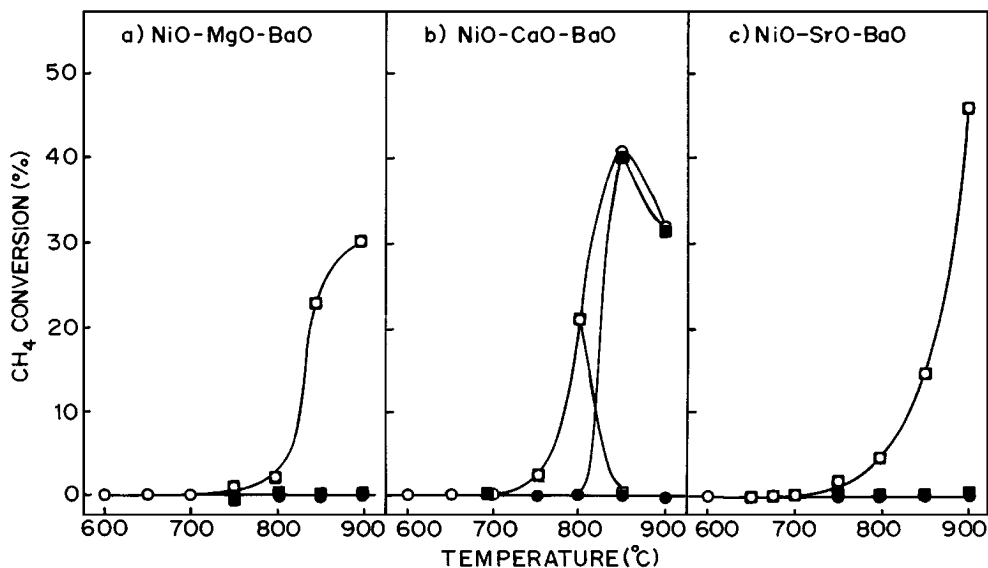


FIG. 3. Temperature-programmed reaction of methane with NiO-MgO-BaO, NiO-CaO-BaO, and NiO-SrO-BaO catalysts in the absence of free-O<sub>2</sub> (conversion of methane—total (○), to CO<sub>2</sub> (●), to CO (■), and to adsorbed carbon species (□)).

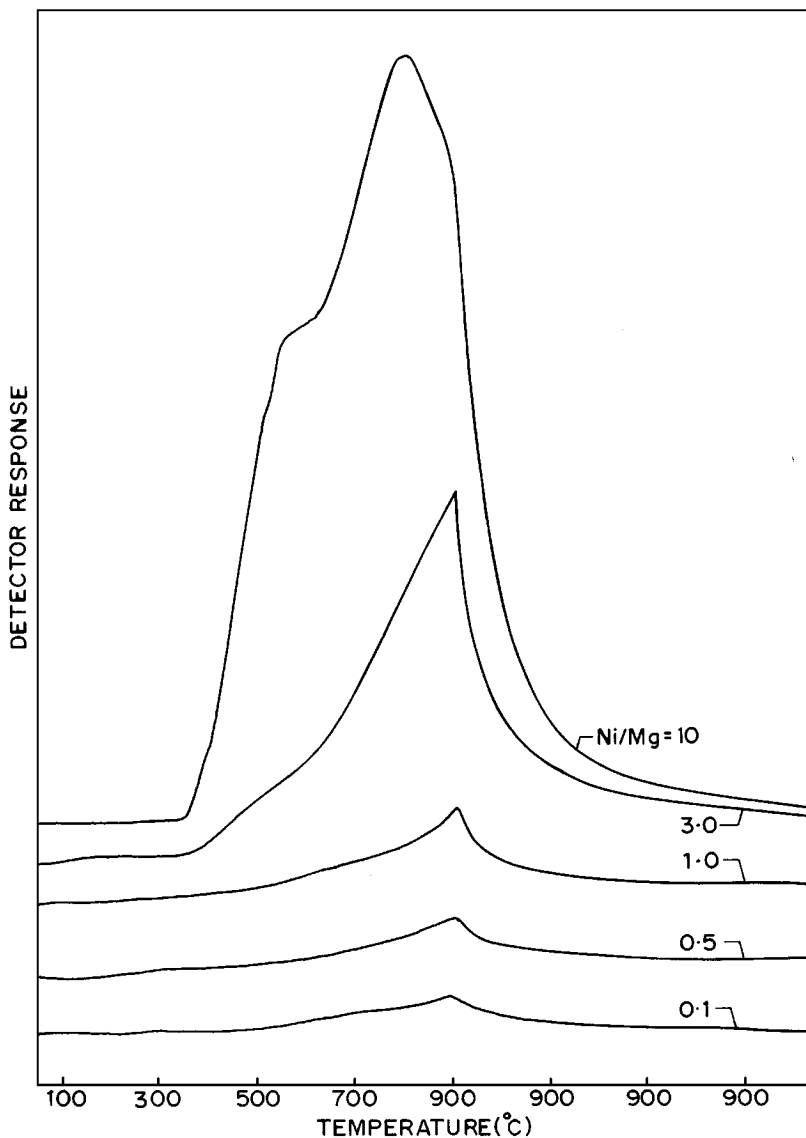


FIG. 4. Temperature-programmed reduction by  $H_2$  of NiO-MgO with different Ni/Mg ratios.

TABLE 2

Surface Area and TPR Peak Maximum Temperatures for the NiO-Containing Alkaline Earth Metal Oxide Catalysts (Ni/Alkaline Earth(s) = 1.0)

Catalyst	Surface area ( $m^2 \cdot g^{-1}$ )	Peak maximum temperature ( $^{\circ}C$ )	
		1st peak	2nd peak
NiO-MgO	5.3	>900	—
NiO-CaO	2.1	490	800 (small hump)
NiO-SrO	0.4	450 (minor)	640 (major)
NiO-MgO-CaO	2.8	550 (small hump)	>900
NiO-MgO-SrO	1.0	500 (major)	$\geq 900$ (minor)
NiO-MgO-BaO	0.8	525 (major)	850 (minor)
NiO-SrO-BaO	0.3	450 (minor)	570 (major)

than that for those containing alkaline earth oxide(s) other than MgO (Table 2).

Data on the degree of reduction of the NiO from the catalysts in their TPR experiment (i.e. after their reduction by  $H_2$  at  $900^{\circ}C$ ) are given in Table 3. The degree of reduction of NiO from the NiO-MgO is lowest (8.0%) and that from NiO-SrO and NiO-SrO-BaO is highest (100%). The degree of NiO reduction for NiO-MgO is increased by adding other alkaline earth oxides to this catalyst. Whereas, the degree of NiO reduction for the NiO-CaO and NiO-SrO catalysts is decreased markedly due to the addition of MgO in these catalysts, due to the solid solution of part of the NiO in the MgO.

It may be noted that the surface area of the NiO-containing catalysts is strongly influenced by the presence

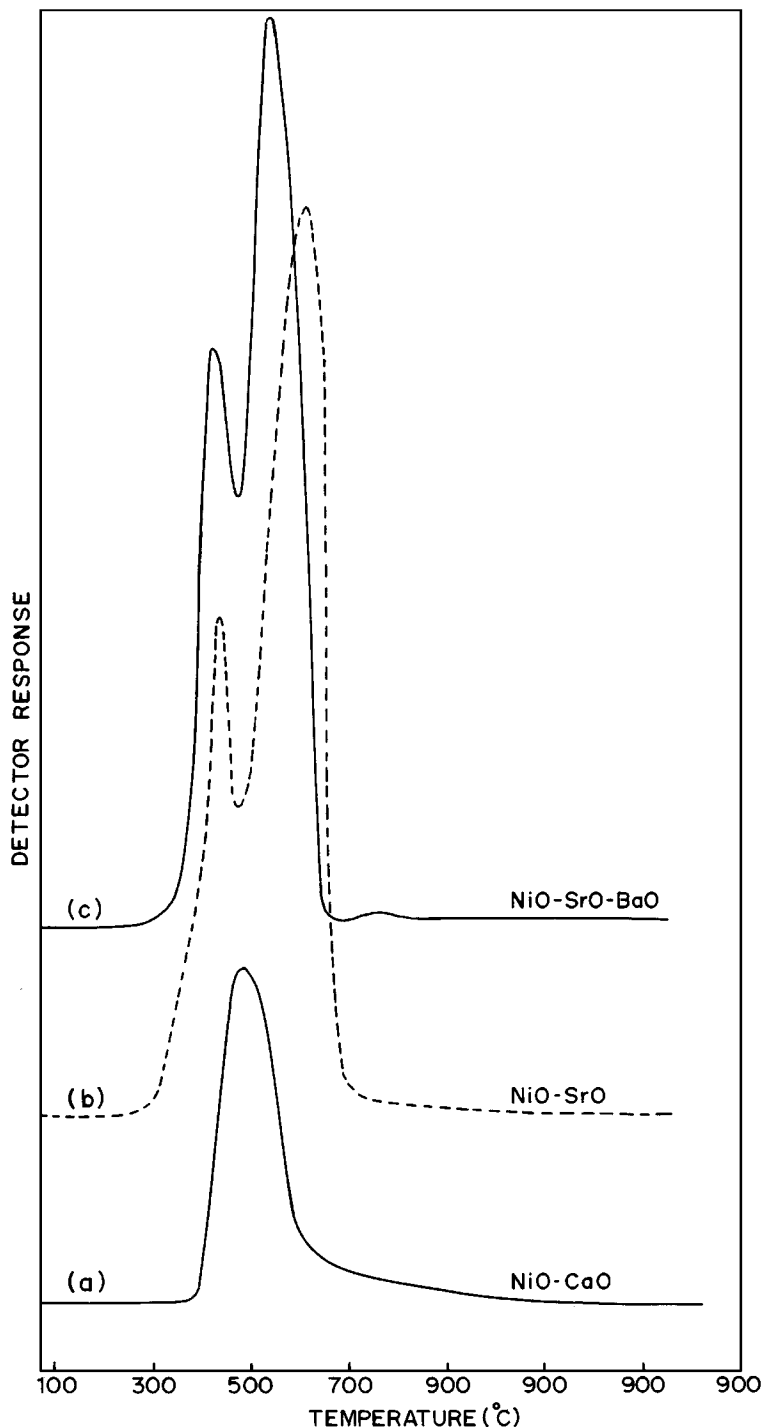


FIG. 5. Temperature-programmed reduction by  $H_2$  of NiO-CaO, NiO-SrO, and NiO-SrO-BaO catalysts.

of a particular alkaline earth oxide in the catalyst (Table 2). The surface area of the catalyst containing the different alkaline earth oxide(s) is in the following order:  $MgO > CaO > SrO > BaO$ . Thus, the catalyst sintering is low in the presence of MgO but high in the presence of SrO and/or BaO.

#### *Characterization of Reduced Catalysts by XRD and XPS*

The NiO-alkaline earth oxide(s) catalysts are reduced by  $H_2$  (30%  $H_2$  in  $N_2$ ) at 500°C for 1 h, passivated by treating them with  $O_2$  (1 mol%  $O_2$  in  $N_2$ ) at room temperature and

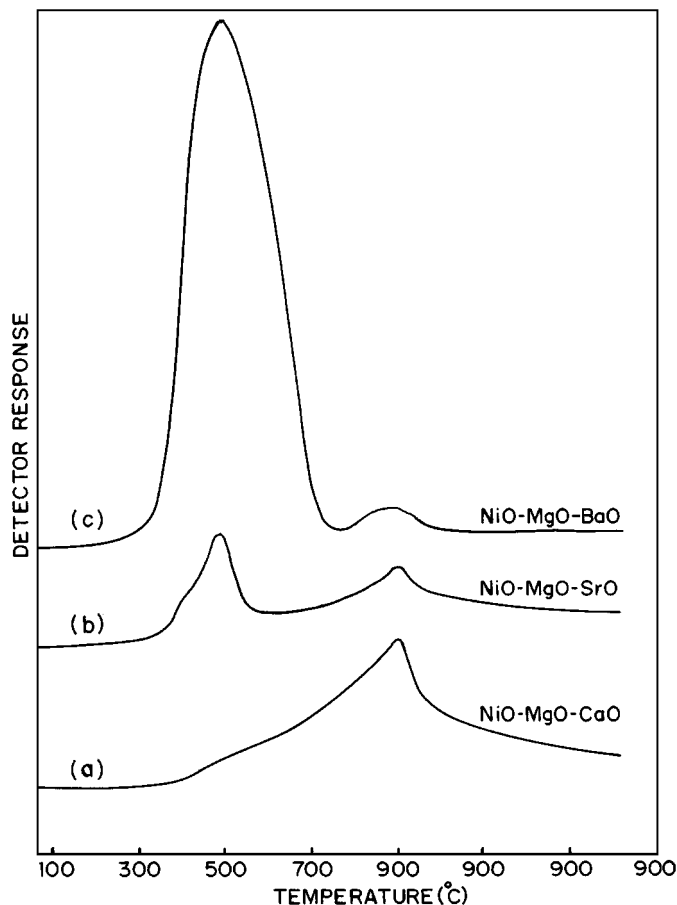


FIG. 6. Temperature-programmed reduction by  $H_2$  of NiO-MgO-CaO, NiO-MgO-SrO, and NiO-MgO-BaO catalysts.

then characterized by XRD for their NiO and  $Ni^0$  phases and by XPS for their surface concentration of nickel and alkaline earth(s).

The XRD spectra (for  $2\theta = 42^\circ$ – $46^\circ$ ) of the reduced catalysts are compared with that of the unreduced catalysts in Fig. 7. All the reduced catalysts show the presence of metallic Ni ( $Ni^0$ ) (XRD peak at  $2\theta = 44.3 \pm 0.1^\circ$ ). However,

TABLE 3

Degree of Reduction of the NiO from Ni-Containing Alkaline Earth Oxide Catalysts in Their Temperature Programmed Reduction

Catalyst	Amount of hydrogen consumed ( $mmol \cdot g^{-1}$ )	Degree of reduction (%)
NiO-MgO	0.7	8.0
NiO-CaO	3.3	43.4
NiO-SrO	5.6	100.0
NiO-MgO-CaO	1.4	17.0
NiO-SrO-CaO	5.6	86.7
NiO-MgO-SrO	1.1	16.0
NiO-MgO-BaO	4.4	75.9
NiO-SrO-BaO	5.0	100.0

the XRD peak for  $Ni^0$  for the reduced NiO-MgO, NiO-MgO-CaO, and NiO-MgO-SrO catalysts is small and that for the reduced NiO-CaO, NiO-MgO-BaO, and NiO-SrO-BaO catalysts is large. This is consistent with the observed reducibility of these catalysts (Table 3).

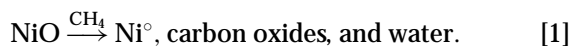
The XPS results in Table 4 reveal that the surface concentration of Ni relative to that of alkaline earth element(s) is decreased markedly after the reduction of all the catalysts. The decrease is, however, very large for the NiO-SrO and all the BaO containing catalysts. The oxidation state of nickel present on the surface of reduced and unreduced catalysts is zero and two, respectively.

## DISCUSSION

The NiO-alkaline earth oxide(s) catalysts, reduced by  $H_2$  at  $500^\circ C$  and  $900^\circ C$ , show their activity in the methane-to-syngas conversion reaction in the following order: NiO-MgO ( $500^\circ C$ ) > NiO-MgO-CaO ( $500^\circ C$ ) > NiO-CaO ( $500^\circ C$ ) > NiO-MgO-SrO ( $900^\circ C$ ) > NiO-MgO-SrO ( $500^\circ C$ ) > NiO-CaO-SrO ( $500^\circ C$ ) > NiO-CaO-SrO ( $900^\circ C$ ) > NiO-SrO ( $900^\circ C$ ) > NiO-MgO-BaO ( $900^\circ C$ ) > NiO-SrO ( $500^\circ C$ )  $\geq$  NiO-MgO-BaO ( $500^\circ C$ ) and NiO-CaO-BaO and NiO-SrO-BaO ( $500^\circ C$  or  $900^\circ C$ ). (The temperature in the bracket is the catalyst reduction temperature.)

The highest activity/selectivity shown by the NiO-MgO catalyst is attributed to the incorporation of  $Ni^{+2}$  in the MgO matrix forming a solid solution of NiO in MgO. At the high calcination temperature ( $930^\circ C$ ), a complete solid solution of NiO in MgO is formed (13). In the reduction, the outermost  $Ni^0$  atoms nucleate to form fine metal particles but some, which lie deeper, remain isolated in the MgO matrix, either as  $Ni^0$  or as Ni ions in a low oxidation state. The reduced solid solution provides a strong ionic environment at the metal particle-support interface and even more so for the reduced species ( $Ni^0$ ) which are at the surface but not fully exposed (11). Because of this, there is a higher stability of nickel against sintering for the catalyst with MgO. In the case of this catalyst, the reduction of NiO, which lies deeper in the MgO matrix, occurs only at higher temperatures (Figs. 1a and 4) and, also, the degree of reduction is low (Table 3) because of the incorporation of  $Ni^{+2}$  deep in the MgO matrix. The TPR of NiO-MgO (Fig. 4) is quite similar to that observed for a typical NiO-MgO complete solid solution (11,14).

It may be noted that although the reduction of NiO from NiO-MgO at  $500^\circ C$  is very low (Figs. 4 and 7), the catalyst shows high activity/selectivity because of the reduction of NiO present at the external surface and in the upper layer of the catalyst particles by the following reactions at the higher reaction temperature during the short initial reaction period:



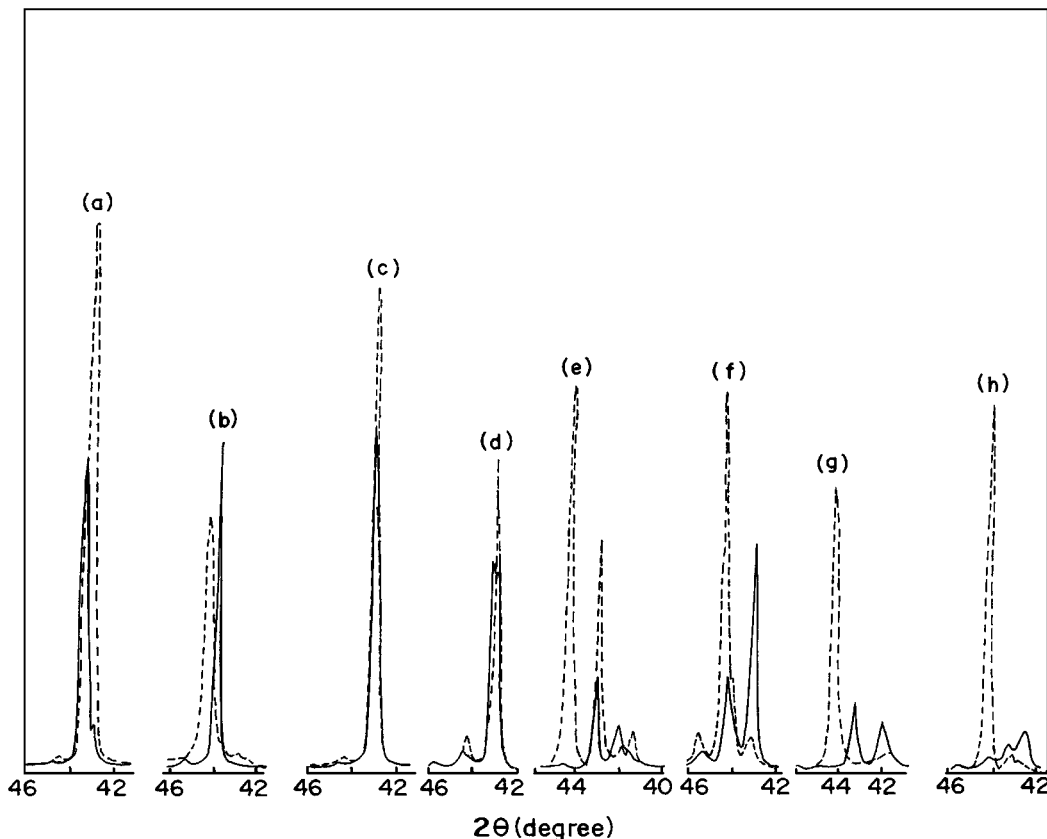
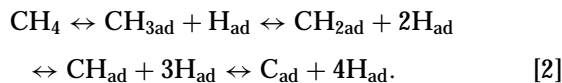
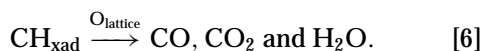


FIG. 7. XRD spectra for  $2\theta = 42\text{--}46^\circ$  of the different NiO-alkaline earth oxide(s) catalysts before reduction (—) and after reduction (---) by  $\text{H}_2$  at  $500^\circ\text{C}$  for 1h: (a) NiO-MgO; (b) NiO-CaO; (c) NiO-MgO-CaO; (d) NiO-MgO-SrO; (e) NiO-MgO-BaO; (f) NiO-CaO-SrO; (g) NiO-CaO-BaO; (h) NiO-SrO-BaO ( $\text{Ni}^{\text{i}}$  and NiO correspond to the peaks at  $2\theta = 44.2^\circ$  and  $43.6^\circ$ , respectively).

In the temperature-programmed reaction of pure methane with the NiO-MgO catalysts, methane is converted mainly into the carbon species retained or adsorbed on the catalyst. The formation of these species is expected by the dissociative adsorption of methane on metallic nickel (15,16) as



The CO and  $\text{CO}_2$  in the methane conversion reaction are expected to be formed by the reactions of adsorbed carbon or  $\text{CH}_x$  species with the lattice oxygen:



In the presence of free-  $\text{O}_2$ , the conversion of methane to CO and  $\text{CO}_2$  over the catalyst is also expected to occur

according to the above reactions, except for the fact that the lattice oxygen ( $\text{O}_{\text{lattice}}$ ) is replaced by adsorbed oxygen ( $\text{O}_2 \leftrightarrow 2\text{O}_{\text{ad}}$ ) and  $\text{H}_2$  is formed by the combinative desorption of the adsorbed hydrogen.

The NiO-CaO catalyst also shows high activity/selectivity in the oxidative methane-to-syngas conversion process (Table 1). It also reacts with pure methane, yielding CO and/or  $\text{CO}_2$  with high conversion even at  $\leq 700^\circ\text{C}$  (Fig. 1b); the formation of adsorbed carbon species in this case is, however, observed at the higher temperatures. The maximum observed for the methane conversion (Fig. 1b) is due to the depletion of the lattice oxygen from the NiO of the catalyst. The reduction of NiO from this catalyst by  $\text{H}_2$  (Fig. 5a) also occurs to an appreciable extent at the lower temperatures (below  $600^\circ\text{C}$ ). However, the observed low degree of reduction (43.4%) in the TPR indicates that a part of NiO is buried deep in the CaO lattice, forming a solid solution of the NiO in CaO, similar to that observed earlier (17). The observed small hump at about  $800^\circ\text{C}$  in the TPR curve (Fig. 5a) is due to the reduction of the NiO in the CaO matrix at the external surface. The addition of MgO to this catalyst causes a small but significant improvement in its catalytic performance (Table 1) due to the



TABLE 4

Surface Composition of the Ni-Containing Alkaline Earth Oxide Catalysts without or with Reduction (at 500°C by H<sub>2</sub> for 1 h)

Catalyst	Reduced or unreduced	Surface composition of Ni and alkaline earth elements	Ni/alkaline earth element(s) (mole ratio)
NiO-MgO	Reduced	Ni = 15.3% Mg = 84.7%	Ni/Mg = 0.18
NiO-CaO	Unreduced	Ni = 56.3%, Ca = 43.7%	Ni/Ca = 1.29
	Reduced	Ni = 28.0%, Ca = 72.0%	Ni/Ca = 0.39
NiO-SrO	Unreduced	Ni = 20.5%, Sr = 79.5%	Ni/Sr = 0.26
	Reduced	Ni = 2.0%, Sr = 98.0%	Ni/Sr = 0.02
NiO-CaO-MgO	Reduced	Ni = 19.7%, Ca = 42.2%, Mg = 38.1%	Ni/(Mg + Ca) = 0.24
NiO-MgO-SrO	Unreduced	Ni = 43.6%, Mg = 32.1%, Sr = 24.3%	Ni/(Mg + Sr) = 0.77
	Reduced	Ni = 17.6%, Mg = 36.3%, Sr = 46.1%	Ni/(Mg + Sr) = 0.21
NiO-CaO-SrO	Unreduced	Ni = 16.1%, Ca = 25.1%, Sr = 58.8%	Ni/(Ca + Sr) = 0.19
	Reduced	Ni = 6.0%, Ca = 32.0%, Sr = 62.0%	Ni/(Ca + Sr) = 0.06
NiO-MgO-BaO	Unreduced	Ni = 7.6%, Mg = 49.9%, Ba = 42.5%	Ni/(Mg + Ba) = 0.08
	Reduced	Ni = <0.01%, Mg = <0.01%, Ba = 100.0%	Ni/(Mg + Ba) = <0.01
NiO-CaO-BaO	Unreduced	Ni = 41.7%, Ca = 26.8%, Ba = 31.5%	Ni/(Ca + Ba) = 0.71
	Reduced	Ni = <0.01%, Ca = 42.8%, Ba = 57.2%	Ni/(Ca + Ba) = <0.01
NiO-SrO-BaO	Unreduced	Ni = 14.8%, Sr = 70.9%, Ba = 14.3%	Ni/(Sr + Ba) = 0.17
	Reduced	Ni = 0.0%, Sr = 77.3%, Ba = 22.7%	Ni/(Sr + Ba) = <0.01

formation of NiO-MgO solid solution in the presence of CaO and consequently the degree of NiO reduction is also decreased from 43.4% to 17.0% (Table 3).

The NiO-SrO catalyst reduced at 500°C is not active and selective in the process but its performance is improved

after the reduction at higher temperature (900°C) (Table 1). This is consistent with the fact that the NiO from this catalyst is reduced at the higher temperature, as indicated by the high peak maxima temperature (640°C) of the major TPR peak (Fig. 5b) and is also consistent with its reactivity with pure methane to an appreciable extent only at higher temperatures (above 800°C) (Fig. 1c). The addition of MgO or CaO to this catalyst results in the improvement in its catalytic performance in the oxidative conversion of methane to syngas (Table 1) and also in its reaction with pure methane (Figs. 2a and 2b). Because of the addition of MgO, a part the NiO forms a solid solution with MgO, resulting in a decrease in the degree of reduction (Table 3) and also an increase in the peak maximum temperature of both the TPR peaks (Table 2); the relative size of the two peaks is also changed. The formation of solid solution of NiO in MgO is responsible for the observed higher activity of the NiO-SrO-MgO catalyst when compared with that of the NiO-SrO-CaO catalyst (Table 1).

The addition of BaO to the NiO-MgO or NiO-CaO or NiO-SrO catalyst results in a complete deactivation of the catalyst for the catalytic process. This is so even when the degree of reduction of the NiO from these catalysts is high (Table 3). For these catalysts (except NiO-CaO-BaO), the reactivity of pure methane is low and also there is no formation of CO or CO<sub>2</sub> even at 900°C in their temperature-programmed reaction with the methane (Fig. 3).

The two peak maxima observed in the TPR of SrO and/or BaO containing catalysts (Figs. 5 and 6) suggest that the NiO in these catalysts exists in two different forms—the first one is easy to reduce (which is reducible at low temperature) and second one is difficult to reduce (which is reducible only at a higher temperature). The first form of the NiO is expected to be free NiO in the catalysts, whereas the second form of NiO is the NiO dissolved in the matrix of MgO and/or that interacting strongly with the other alkaline earth oxides present in the catalyst. A comparison of the TPR curves in Fig. 6 shows that the formation of the solid solution of NiO in MgO is not affected in the presence of CaO but it is decreased markedly due to the presence of SrO or BaO in the catalyst.

It is interesting to note that although the SrO and BaO containing catalysts (reduced at 500°C) contain a high concentration of metallic nickel (Ni<sup>0</sup>) (Fig. 7), relative to that of NiO, these catalysts show poor activity/selectivity and, in the absence of MgO and CaO, show almost no activity in the oxidative conversion of methane to syngas (Table 1). The observed little or no catalytic activity of these SrO or BaO containing catalysts (after the reduction at 500°C) is quite consistent with the extremely low concentration of nickel on the catalyst surface (Table 4). The observed large decrease in the surface concentration of nickel after the catalyst reduction could be because of heavy sintering or crystal growth of metallic nickel and/or the coverage of the

metallic nickel particles by the SrO and/or BaO, somewhat similarly to the decoration effect observed earlier in the case of reduced TiO<sub>2</sub>-containing noble metals (18). However, for confirming this and having a better understanding, further studies are essential. It may be noted that the sintering of the catalyst during its preparation/calciatiion is higher when it contains strontium and/or barium compounds, as indicated by the observed surface area of the catalysts (Table 2).

### CONCLUSIONS

From this investigation, the following general conclusions can be drawn about the surface properties and catalytic activity/selectivity in the partial oxidation of methane to syngas over the NiO-alkaline earth oxide(s) catalysts:

(1) The surface area, reduction by H<sub>2</sub> or reducibility of NiO, surface composition of nickel, relative to that of alkaline earth(s) before and after the reduction by H<sub>2</sub> at 500°C, reaction with pure methane (before the reduction) and catalytic activity/selectivity in the oxidative methane-to-syngas conversion of the NiO-alkaline earth oxide(s) catalysts are strongly influenced by the alkaline earth oxide(s) present in the catalyst.

(2) The catalyst sintering is increased because of the addition of higher alkaline earth oxide(s) to NiO.

(3) The reducibility by H<sub>2</sub> of the NiO from the catalyst is lowest for the MgO-containing catalysts and highest for the SrO and/or BaO containing catalysts. The NiO forms a complete solid solution with MgO but its solution with CaO is partial. For the SrO and/or BaO containing NiO catalysts, the NiO exists in two different forms—easily reducible (i.e. free-NiO) and difficult to reduce (i.e. NiO interacting strongly with alkaline earth oxide(s)).

(4) In the temperature-programmed reaction of pure methane, the NiO-CaO catalyst shows the highest reactivity and the other catalysts show appreciable reactivity only at higher temperatures (above 750°C).

(5) The surfaceNi/alkaline earth(s) ratio for all the catalysts is decreased due to their reduction by H<sub>2</sub>; the decrease is, however, very large for the NiO-SrO and all the BaO containing catalysts. Consequently, these catalysts show little or no activity in the oxidative conversion of methane to syngas.

(6) Among the alkaline earth oxide(s) containing NiO catalysts, the NiO-CaO, NiO-MgO-CaO, and NiO-MgO

catalysts show increasingly superior performance in the oxidative methane-to-syngas conversion. However, the addition of SrO or BaO to the NiO-MgO or NiO-CaO catalysts causes a drastic reduction in the catalytic activity/selectivity.

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