

Oxidative Conversion of Methane to Syngas over Nickel Supported on Commercial Low Surface Area Porous Catalyst Carriers Precoated with Alkaline and Rare Earth Oxides

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Partial oxidation of methane to CO and H₂ at very small contact times (4.8 ms at STP) over different supported Ni-catalysts at 700 and 800°C, CH₄/O₂ ratio in feed of 1.8 and gas space velocity of $5.2 \times 10^5 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ (at STP) has been investigated. The catalysts were prepared by depositing NiO–MgO on different commercial low surface area porous catalyst carriers (obtained from M/S Norton Co., USA) consisting of refractory compounds (viz. SiO₂, Al₂O₃, SiC, ZrO₂, and HfO₂) at different concentrations and having different surface properties and also prepared by depositing NiO on the catalyst carriers precoated with different alkaline and rare earth oxides (viz. MgO, CaO, SrO, BaO, Sm₂O₃, and Yb₂O₃). The catalysts have been characterized by their TPR by H₂ from 100 to 900°C, degree of NiO reduction, and H₂ chemisorption after the catalyst reduction at 900°C. The influence of support (its composition and surface properties), method of NiO and MgO deposition, support precoating agent, loadings of NiO and MgO (as support precoating agent), and calcination temperature on the conversion and selectivity has been studied. The influence of these catalyst parameters on the TPR, degree of NiO reduction, and H₂ chemisorption on the catalyst has also been studied. The catalyst characteristics are strongly influenced by the support (containing Al₂O₃ and/or SiO₂ at higher concentrations and having higher surface area), precoating agent, loading of MgO precoat on the support, particularly at lower loadings (below 2 wt%), and also by the catalyst calcination temperature above 900°C. The catalyst prepared by depositing NiO on the commercial supports (except SA-5552 having much higher surface area) precoated with MgO ($6 \pm 1 \text{ wt}\%$) and calcined at 900°C shows excellent performance in the catalytic process (at 800°C) with very high methane conversion (>91%), selectivity (>95%) and CO productivity (>13 mol · g⁻¹ · h⁻¹, which is about two orders of magnitude higher than that obtained in steam reforming of methane). However, the conversion and selectivity are reduced drastically when the MgO loading is decreased below 2 wt%, the MgO precoat is replaced by that of SrO or BaO or when the catalyst is calcined above 1050°C.

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INTRODUCTION

Catalytic oxidative conversion of methane to syngas with H₂/CO ratio of 2.0, a versatile feedstock for the methanol and Fischer–Tropsch synthesis processes, is a process of great commercial importance. Since the last few years, extensive efforts have been made for converting methane by its partial oxidation with oxygen to syngas, using different nickel, cobalt, and noble metal-containing catalysts (1–15).

NiO–MgO (6), NiO–CaO (7), and NiO–Yb₂O₃, or other rare earth oxide (8) catalysts show high activity and selectivity at very low contact time (1–10 ms) and, hence, show very high productivity in the oxidative conversion of methane to syngas. However, because of their hygroscopic nature, the pellets of these composite mixed metal oxide catalysts have poor mechanical strength (i.e., low crushing strength and poor attrition resistance). The mechanical strength of a catalyst can be improved by supporting it on a porous catalyst carrier having high mechanical strength. But when the above three mixed metal oxide catalysts were deposited on a sintered low surface area porous silica–alumina catalyst carrier, the activity of the catalysts was reduced very significantly (15). This was due to the formation of NiAl₂O₄ (spinel), which is catalytically inactive and also very difficult to reduce, by a solid–solid reaction between NiO (from catalyst) and Al₂O₃ (from support).

In our recent preliminary studies (14), supported nickel catalysts prepared using commercial sintered low surface-area porous catalyst carriers (containing Al₂O₃ and/or SiO₂) precoated with MgO, CaO, or rare-earth oxide show very much higher activity, selectivity, and productivity in the oxidative conversion of methane to syngas than the catalysts prepared using the catalyst carriers without any precoating. The beneficial effect of the support precoating was attributed to the elimination or drastic reduction in the formation of catalytically inactive NiAl₂O₄ (spinel) and/or Ni₂SiO₄ phases resulting from the chemical interactions between NiO and Al₂O₃ and/or SiO₂ from support at high catalyst calcination temperature. It is, therefore, interesting to investigate in detail the effects of various parameters of

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the preparation of supported nickel catalyst (viz., use of different low surface area porous catalyst carriers, method of deposition, precoating agents, loading of precoating agent, loading of NiO, and catalyst calcination temperature) on (1) temperature programmed reduction (TPR), (2) degree of reduction of nickel oxide from the catalyst, (3) chemisorption of hydrogen (which is a measure of Ni surface area) on the catalyst after its reduction, and (4) conversion and selectivity of the supported Ni catalysts in the partial oxidation of methane to syngas at very low contact time (4.8 ms at STP). The present investigation was undertaken with these objectives.

EXPERIMENTAL

Unsupported NiO-MgO with Ni/Mg ratio of 3.0 (Table 1) was prepared as per the procedure reported earlier (7). NiO-MgO (Ni/Mg = 3.0) directly supported on different low surface area ($<1 \text{ m}^2 \cdot \text{g}^{-1}$) porous catalyst carriers (SA-5205, SA-5218, SA-5552, SC-5532, SS-5231, and SZ-5564, obtained from M/S Norton Co., USA) were prepared by impregnating (using the incipient wetness impregnation technique) 22–30 mesh-size particles of the commercial supports with mixed nickel nitrate and magnesium nitrate solutions, drying and calcining in air at 900°C for 4 h; NiO supported on the different catalyst carriers precoated with different alkaline earth or rare-earth oxides were prepared

TABLE 1

Results of the Oxidative Conversion of Methane to CO and H_2 over NiO-MgO (Ni/Mg = 3.0) Mixed Metal Oxides Deposited on the Different Supports (Loading of NiO-MgO on Support = $13 \pm 1 \text{ wt}\%$)

Support	Catalyst surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	Reaction temp. ($^\circ\text{C}$)	CH_4 convn. (%)	Selectivity (%)		H_2/CO ratio	Productivity for CO ($\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$)
				CO	H_2		
Nil	3.66	800	95.9	99.8	99.6	2.00	14.3
		700	90.9	96.6	94.0	1.95	13.1
SA-5205	0.39	800	86.5	96.4	92.7	1.92	12.4
		700	80.3	92.2	90.9	1.97	11.1
SA-5218	0.34	800	82.8	95.9	92.1	1.92	11.9
		700	81.1	93.8	91.6	1.95	11.4
SA-5552	0.89	900	41.2	91.0	35.4	0.78	5.6
		800	1.8	—	—	—	—
SC-5532	0.36	900	1.9	—	—	—	—
		800	No reaction				
SZ-5564	0.57	800	86.2	95.7	92.5	1.93	12.3
		700	83.2	93.4	90.4	1.94	11.6
SS-5231	0.88	800	56.7	86.9	73.6	1.69	7.4

Note. Reaction conditions: $\text{CH}_4/\text{O}_2 = 1.8$ and GHSV = $5.2 \times 10^5 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$.

TABLE 2

Support	Main components (wt%)					Surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \cdot \text{g}^{-1}$)	Porosity (%)
	Al_2O_3	SiO_2	SiC	$\text{HfO}_2 + \text{ZrO}_2$				
SA-5552	93.1	5.6	—	—		0.33	0.39	59
SA-5205	86.1	11.8	—	—		<0.05	0.35	54
SA-5218	86.1	12.0	—	—		<0.05	0.20	40
SC-5532	4.7	28.5	65.8	—		0.15	0.23	45
SS-5231	4.1	95.0	—	—		0.22	0.25	35
SZ-5564	0.4	1.6	—	94.1		0.10	0.15	45

by impregnating nickel nitrate from its aqueous solution on 22–30 mesh-size particles of the precoated catalyst carriers, using incipient wetness impregnation technique, drying and calcining in air at different temperatures ($600\text{--}1200^\circ\text{C}$) for 4 h. The catalyst carriers were precoated with alkaline earth or rare-earth oxide by impregnating the carriers with the corresponding metal nitrate, drying, and calcining in air at 900°C for 4 h.

The main chemical constituents, surface area, pore volume, and porosity of the different commercial catalyst carriers are as shown in Table 2. The catalyst carriers were crushed to 22–30 mesh-size particles before using them for supporting the catalysts.

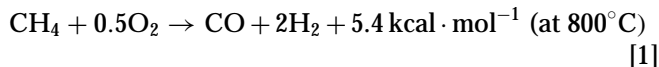
The catalysts were characterized for their surface area by the single point BET method, using a Monosorb Surface Area Analyser (Quantachrome Corp., USA). The catalysts were also characterized by their temperature programmed reduction (TPR) from 100 to 900°C with a linear heating rate of $20^\circ\text{C} \cdot \text{min}^{-1}$ in a flow of $\text{H}_2\text{--Ar}$ (3.7 mol% H_2) mixture (space velocity = $6000 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$) in a quartz reactor (ID 4 mm) having a low dead volume. The hydrogen consumed in the TPR was measured quantitatively by TCD. Before the TPR, the catalyst was pretreated in a flow of He at 900°C for 1 h. The chemisorption of H_2 on the reduced catalysts was measured by saturating the catalyst with H_2 at 50°C in a flow of the $\text{H}_2\text{--Ar}$ mixture for 4 h and then carrying out the temperature-programmed desorption (TPD) of the adsorbed hydrogen from 50 to 700°C at a linear heating rate at $10^\circ\text{C} \cdot \text{min}^{-1}$ in the flow of the $\text{H}_2\text{--Ar}$ mixture (space velocity = $6000 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$). The hydrogen desorbed (which corresponds to the amount adsorbed at 50°C) was measured quantitatively by the TCD. The H_2 desorption was complete upto 700°C .

The catalytic partial oxidation of methane to syngas was carried out by passing continuously a gaseous feed containing pure methane ($>99.95\%$) and oxygen ($>99.9\%$) over the catalyst (0.02 g) packed in a quartz reactor (ID 4 mm) kept in a tubular furnace (ID 25 mm). The 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 analysed by an on-line gas chromatograph using a spherocarb column.

RESULTS AND DISCUSSION

The partial oxidation of methane to syngas,



at very small contact time ($\text{GHSV} = 5.2 \times 10^5 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$) has been carried out over the following nickel containing catalysts with or without support at atmospheric pressure at two different temperatures (700 and 800°C):

- NiO-MgO (Ni/Mg = 1.2 and 3.0) without any support.
- Mixed NiO-MgO (Ni/Mg = 3.0) supported on different commercial catalyst carriers, commonly used for supporting oxidation catalysts.
- NiO supported on the catalyst carriers which are pre-coated with MgO.
- NiO supported on a particular catalyst carrier (SA-5205) pre-coated with different alkaline earth and rare earth oxides.
- NiO supported on SA-5205 pre-coated with MgO (NiO/MgO/SA-5205) with different loadings of MgO and NiO.
- NiO/MgO/SA-5205 catalyst (Loading of NiO and MgO = 13.6 and 5.1 wt%, respectively) calcined at different temperatures (600–1200°C).

The commercial catalyst carriers used for the supported nickel catalysts (Tables 1 and 3) are sintered low surface area, porous supports composed of refractory compounds, such as Al_2O_3 , SiO_2 , SiC , ZrO_2 , and HfO_2 , etc. They have different chemical compositions and surface properties (viz., surface area, pore volume, and porosity), as described earlier. The catalysts in their operating state (i.e., in their active form) are essentially Ni^0 dispersed on the alkaline earth and rare earth oxides supported on the different supports. The NiO from the catalysts is reduced in the initial short reaction period by its autocatalytic reaction with methane (6–8).

The catalysts have been characterized for their specific surface area. The reducibility (at different temperatures) and degree of reduction of the NiO supported on different catalyst carriers pre-coated with alkaline earth or rare earth oxides have been determined by carrying out TPR of the catalysts by H_2 (3.7 mol% H_2 in Ar) from 100 to 900°C at a linear heating rate of $20^\circ\text{C} \cdot \text{min}^{-1}$. The degree of NiO reduction is determined from the concentration of NiO in the catalyst and the amount of H_2 consumed in the TPR, assuming the reaction stoichiometry ($\text{NiO} + \text{H}_2 \rightarrow \text{Ni}^0 + \text{H}_2\text{O}$). The reduced catalysts are characterized by the chemisorption of H_2 at 50°C.

TABLE 3

Results of the Oxidative Conversion of Methane to CO and H_2 over NiO Deposited on the Different Supports Precoated with MgO (Loading of MgO and NiO on Support = 6 ± 1 and 14 ± 2 wt%, Respectively)

Support	Catalyst surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	Reaction temp. ($^\circ\text{C}$)	CH_4 convn. (%)	Selectivity (%)		H_2/CO ratio	Productivity for CO ($\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$)
				CO	H_2		
Without support ^a	—	800	93.5	92.9	96.9	2.07	13.0
		700	88.1	91.5	93.4	2.04	12.0
SA-5205	2.0	800	94.7	97.5	95.6	1.96	13.8
		700	89.7	94.3	95.0	2.01	12.6
SA-5218	1.6	800	92.9	99.8	97.1	1.86	13.9
		700	89.4	97.1	94.7	1.95	12.9
SA-5552	3.2	800	81.4	98.8	97.1	1.97	12.0
		700	78.8	97.5	96.8	1.99	11.5
SC-5532	1.7	800	91.5	96.8	96.1	2.00	13.2
		700	88.9	95.4	95.9	2.01	12.7
SS-5231	3.3	800	91.9	95.1	95.0	2.00	13.0
		700	88.2	92.8	94.0	2.04	12.2
SZ-5563	2.7	800	93.7	97.5	96.7	1.98	13.6
		700	89.5	94.2	94.8	2.01	12.5

Note. Reaction conditions: $\text{CH}_4/\text{O}_2 = 1.8$ and $\text{GHSV} = 5.2 \times 10^5 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$.

^a Unsupported NiO-MgO catalyst having the Ni/Mg ratio (1.2) same as that for the supported catalysts.

Influence of Support

The performance of the supported NiO-MgO (Ni/Mg = 3.0) catalysts in the oxidative conversion of methane to syngas is compared with that of the unsupported NiO-MgO (Ni/Mg = 3.0) in Table 1. The comparison clearly shows a strong influence of support on the performance of NiO-MgO catalyst. Both the conversion and selectivity for the catalyst (NiO-MgO) are decreased after depositing it on the different catalyst carriers. The decrease in the catalytic performance is small when the catalyst is supported on SA-5205, SA-5218, and SZ-5564 supports but it is very large when the catalyst is deposited on the other supports. The catalyst supported on SA-5552 and SC-5532 shows a little or no activity even at 800°C.

However, when the NiO is deposited on the different catalyst carriers pre-coated with MgO, the resulting supported nickel catalysts (Ni/Mg \approx 1.2) show the conversion and selectivity in the catalytic process comparable to or even better (for SA-5205 and SZ-5564 supports) than that observed for the unsupported NiO-MgO (Ni/Mg \approx 1.2) catalyst (Table 3). These results reconfirm the earlier observed beneficial effect of pre-coating of catalyst support (containing Al_2O_3 and SiO_2) with MgO before depositing NiO on the support in the preparation of supported nickel catalyst (14).

The effect of support on the performance of the supported NiO-MgO catalyst (Table 1) arises mainly from the strong chemical interactions between the alumina and/or silica from the supports with the NiO from the mixed NiO-MgO deposited on the supports at the high calcination temperature (900°C). The chemical interactions are expected to result into formation of catalytically inactive binary metal oxide phases such as nickel silicate and/or aluminate, similar to that observed when NiO is directly supported on the silica and/or alumina containing catalyst carriers (14). The chemical interactions are expected to be stronger for the support containing larger concentration of Al_2O_3 and SiO_2 and/or having larger surface area. The results are quite consistent with this. For SZ-5564 support, which contains Al_2O_3 and SiO_2 at low concentrations, the decrease in the catalytic activity is small. For the silica-alumina supports (SA-5205, SA-5218, and SA-5552), the conversion and selectivity observed for the supported Ni-catalyst is decreased with increasing the support surface area. The very low activity of the catalysts supported on high silica containing supports (viz., SS-5232 and SC-5532) may also be due to physical interactions of metal-

lic nickel (formed during the initial period of the catalytic reaction), leading to its rapid crystal growth or sintering. This aspect of catalyst deactivation by support needs further investigation.

When the supports are precoated with MgO, at the high calcination temperature (900°C), there is a solid-solid reaction between the MgO and the Al_2O_3 and SiO_2 from the support surface, forming a stable protective layer of MgAl_2O_4 (spinel) and MgSiO_3 , respectively, at the MgO-support interface (14). This protective layer is responsible for eliminating the chemical interactions between the active components of the supports (viz., Al_2O_3 and SiO_2) and the NiO, after its deposition on the MgO precoated supports.

The TPR curves for the NiO deposited on SA-5205, SA-5552, SS-5231, and SZ-5564 catalyst carriers precoated with MgO are presented in Fig. 1. Data on the degree of reduction of the NiO from the catalysts and H_2 chemisorption on the catalysts, after reduction at 900°C, are given in Table 4.

The TPR of the NiO/MgO/SA-5205 catalyst is started above 400°C; it shows a single peak with a peak maximum

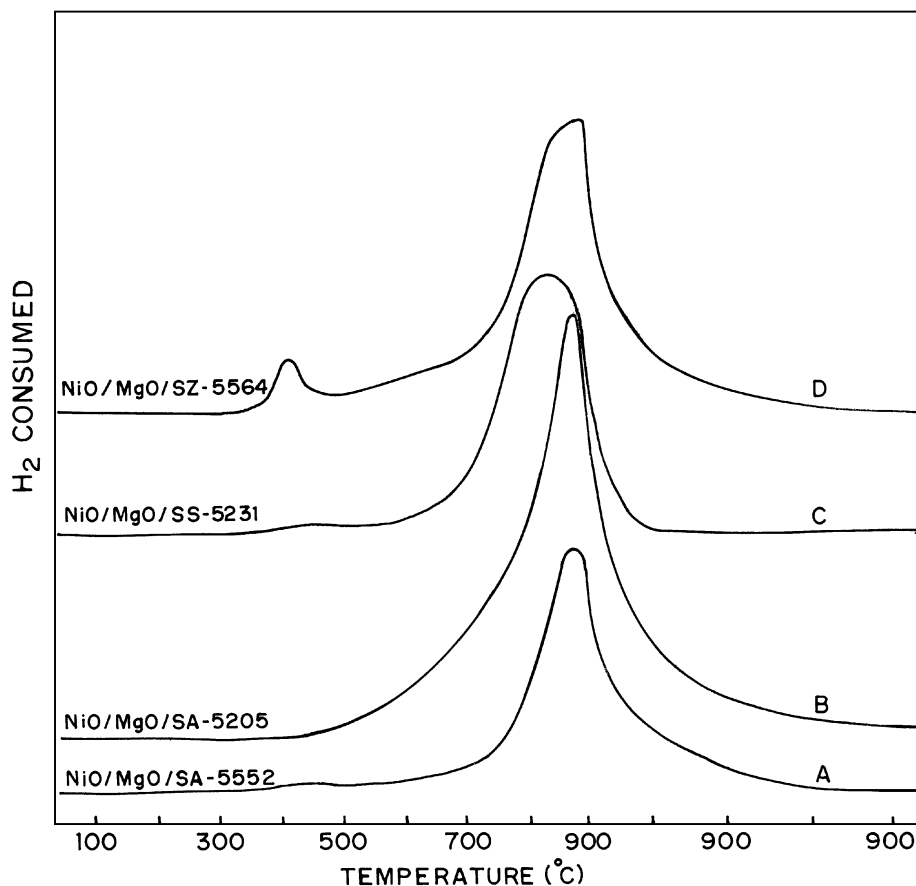


FIG. 1. TPR of nickel oxide supported on different catalyst carriers precoated with MgO (loading of MgO = 6.0 ± 1.0 wt% and loading of NiO = 12.2 ± 1.5 wt%).

TABLE 4

Results Showing the Effect of Support on the Degree of Reduction (by H₂ in TPR) of NiO Deposited on Different Supports Precoated with MgO and H₂ Chemisorption on the Reduced Catalysts (Loading of MgO and NiO: 6 ± 1 and 12.2 ± 1.5 wt%, Respectively)

Support	Reduction (%)	H ₂ chemisorbed (μmol · g ⁻¹)
SA-5205	34.5	9.4
SA-5552	43.3	6.8
SS-5231	40.3	7.5
SZ-5564	36.7	8.9

above 800°C (Fig. 1B). The TPR is quite similar to that observed for a typical NiO–MgO complete solid solution (16, 17). As expected for the solid solution, the degree of NiO reduction is small (34.5%). The high temperature TPR peak for the NiO/MgO/SA-5552, NiO/MgO/SS-5231 and NiO/MgO/SZ-5564 catalysts (Fig. 1A, C, and D) and their low degree of reduction (Table 4) also indicate the formation of NiO–MgO solid solution in these catalysts. However, the observed small TPR peak between 400 and 500°C for these catalyst, indicating the presence of small amounts of free NiO, suggest that the formation of NiO–MgO solid solution is not complete. Thus, the comparison of the TPR and the degree of reduction of the different supported nickel catalysts shows a strong influence of support on the formation of NiO–MgO solid solution and consequently also on the degree of NiO reduction.

The H₂ chemisorption (which is a measure of the surface area of nickel) of the catalyst is also influenced significantly

TABLE 6

Results Showing the Effect of Precoating Agent (MO_x) on the Degree of NiO Reduction (by H₂ in TPR) of NiO/MO_x/SA-5205 Catalysts and H₂ Chemisorption on the Reduced Catalysts (NiO Loading = 14 ± 2 wt%)

Precoating agent (MO _x)	Reduction (%)	H ₂ chemisorbed (μmol · g ⁻¹)
MgO (5.1 wt%)	34.5	9.4
CaO (6.5 wt%)	53.9	5.2
BaO (8.6 wt%)	57.4	1.7
Yb ₂ O ₃ (13.9 wt%)	74.6	6.5

by the support. The methane conversion is consistent with the H₂ chemisorption; it is increased with increasing the H₂ chemisorption.

Influence of Support Precoating Agent

Results of the oxidative methane-to-syngas conversion over the NiO deposited on SA-5205 precoated with different alkaline earth or rare earth oxides are presented in Table 5. Also, results showing the influence of support precoating agent (alkaline earth or rare earth oxide) on the TPR and degree of NiO reduction of the catalysts and on the H₂ chemisorption, after their reduction, are given in Fig. 2 and Table 6.

The results (Table 5) show a very strong influence of the precoating agent on both the conversion and selectivity in the catalytic process. In the absence of the precoating of the support, the catalyst is not at all active and selective. When the support is precoated with SrO or BaO, the

TABLE 5

Results Showing Effect of the Precoating of Catalyst Support SA-5205 with Different Alkaline and Rare Earth Metal Oxides (MO_x) on the Oxidative Conversion of Methane to CO and H₂ over NiO/MO_x/SA-5205 Catalysts (Loading of NiO on Support = 13 ± 1 wt%)

MO _x	Loading of MO _x (wt%)	Catalyst surface area (m ² · g ⁻¹)	Reaction start temp. (°C)	Reaction temp. (°C)	CH ₄ convn. (%)	Selectivity (%)		H ₂ /CO ratio	Productivity for CO (mol · g ⁻¹ · h ⁻¹)
						CO	H ₂		
Without precoating ^a	0.0		>780	800	3.4	12.1	—	—	0.06
MgO	5.0	2.0	635	800	No reaction				
				700	94.7	97.5	95.6	1.96	13.8
				700	89.7	94.3	95.0	2.01	12.6
CaO	6.5	1.3	675	800	82.0	91.9	89.6	1.95	11.2
				700	73.4	87.2	85.8	1.97	9.6
SrO	16.6	0.8	>800	900	4.7	85.7	—	—	0.6
BaO	8.6	0.7	>800	900	6.1	54.0	—	—	0.5
				800	1.6	33.8	—	—	0.1
Sm ₂ O ₃	15.3	0.9	514	800	87.2	93.8	91.2	1.94	12.2
				700	80.6	90.2	88.1	1.95	10.9
Yb ₂ O ₃	19.7	2.1	538	800	88.3	95.5	93.2	1.95	12.6
				700	81.6	93.6	91.9	1.96	11.4

Note. Reaction conditions: CH₄/O₂ = 1.8 and GHSV = 5.2 × 10⁵ cm³ · g⁻¹ · h⁻¹.

^a NiO is deposited directly on the support.

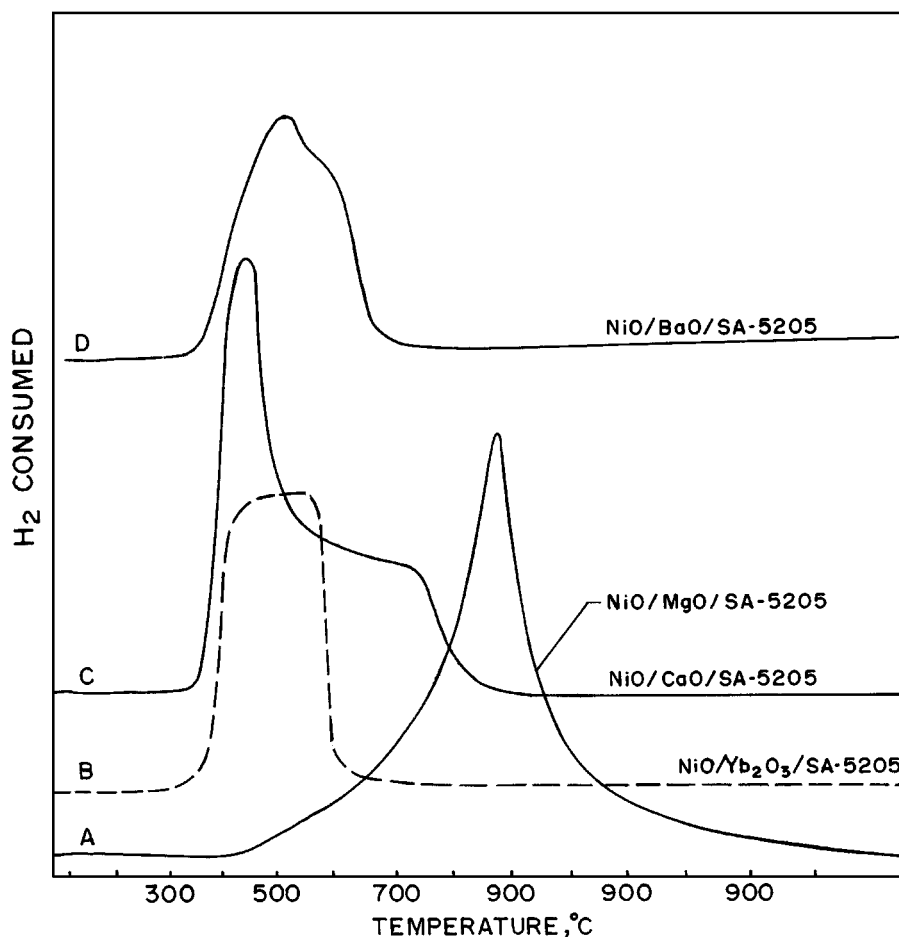


FIG. 2. TPR of nickel oxide supported on catalyst carrier SA-5205 precoated with MgO, CaO, BaO, or Yb₂O₃ (loading of NiO = 12.2 ± 1.5 wt%, loading of MgO, CaO, BaO, and Yb₂O₃ = 5.1, 6.5, 8.6, and 13.9 wt%, respectively).

catalyst shows very poor performance. When the support is precoated with CaO, Sm₂O₃, or Yb₂O₃ the catalyst shows good performance. However, the best performance is observed for the catalyst prepared using MgO as a support precoating agent.

A comparison of the TPR (Fig. 2) and degree of NiO reduction (Table 6) for the catalysts shows a strong influence of the precoating agent on the state of NiO in the catalysts. For MgO as a precoating agent, the NiO reduction occurs at higher temperatures and, also, the degree of reduction is low because of the incorporation of Ni²⁺ deep in the MgO matrix forming NiO–MgO solid solution. However, in the case of other precoating agents, the NiO reduction starts at a lower temperature (below 400°C) and also completes at much lower temperatures; the degree of reduction is also higher. The observed strong influence of the precoating agent on the TPR and degree of reduction of NiO from the supported nickel catalyst (Fig. 2 and Table 6) indicates that the nickel oxide in these catalysts exists in different forms; at least some part of the total NiO exists as free-NiO. The presence of free-NiO was detected by XRD

for the catalysts with CaO, SrO, BaO, Yb₂O₃, and Sm₂O₃ as precoating agents.

It is interesting to note from the results (Table 6) that the degree of NiO reduction for the catalysts with the precoating agent CaO, BaO, and Yb₂O₃ is higher, but the H₂ chemisorption on them (after the reduction) is lower than that for the catalyst with MgO as a precoating agent. The observed lower H₂ chemisorption indicates sintering of nickel in the catalysts. The sintering is highest for the catalyst with BaO as a precoating agent. As expected, this catalyst also shows very poor conversion and selectivity in the oxidative conversion of methane to syngas. The conversion observed for the other catalysts is also consistent with their H₂ chemisorption (Table 5 and 6); it is increased with increasing the H₂ chemisorption. However, interactions of nickel with the precoating agent and/or with the support itself may also be responsible for the observed large variation in the activity of the catalysts.

The observed higher H₂ chemisorption and, hence, higher stability of nickel against sintering for the catalyst with MgO as a precoating agent is attributed to the incorporation of

Ni^{2+} in the MgO matrix forming a solid solution of NiO in MgO. 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 a charged Ni species 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 (16). This is not the case for the $\text{NiO}/\text{Yb}_2\text{O}_3$ catalyst and yet this catalyst shows high conversion and selectivity, although smaller than that shown by the NiO/MgO catalyst. However, the NiO/MgO catalyst is expected to show better stability in the process against sintering. Studies on this aspect are in progress.

Influence of MgO Loading on Support

Results showing the influence of the loading of MgO (which acts as the best precoating agent among the alkaline earth and rare earth oxides) in the catalyst having almost the same NiO loading (13.4 ± 0.2 wt%) on its performance in the partial oxidation of methane are presented in Fig. 3. TPR curves and H_2 chemisorption data for the catalyst with different MgO loading (0–5.1 wt%) are presented in Fig. 4 and Table 7, respectively.

In the absence of MgO, the catalyst shows a very small conversion with very poor selectivity for CO and H_2 . This is expected partly because of the strong chemical interaction of nickel with Al_2O_3 and SiO_2 from the support, resulting in the formation of catalytically inactive binary metal oxide phases, viz., NiAl_2O_4 and Ni_2SiO_4 (14). The degree of NiO reduction at the zero MgO loading is, however, higher than that observed in the presence of MgO. The TPR of the catalyst with zero MgO loading (Fig. 4A) is quite similar to that observed for pure NiO. These observations indicate presence of free-NiO as a major fraction of the total nickel in the catalyst. However, the H_2 chemisorption on the reduced catalyst is very low, indicating sintering of nickel to a large extent. Thus, the very low conversion shown by the catalyst is attributed to both the strong nickel-support chemical interactions and sintering of the active catalyst component (Ni^0).

TABLE 7

Results Showing the Effect of NiO and MgO Loadings on the Degree of NiO Reduction (by H_2 in TPR) of $\text{NiO}/\text{MgO}/\text{SA-5205}$ Catalyst and H_2 Chemisorption on the Reduced Catalyst

Loading (wt%)		Reduction (%)	H_2 chemisorbed ($\mu\text{mol} \cdot \text{g}^{-1}$)
NiO	MgO		
13.2	0.0	64.5	1.1
13.5	2.1	35.0	6.2
13.6	5.1	34.5	9.4
25.7	5.1	42.9	5.7

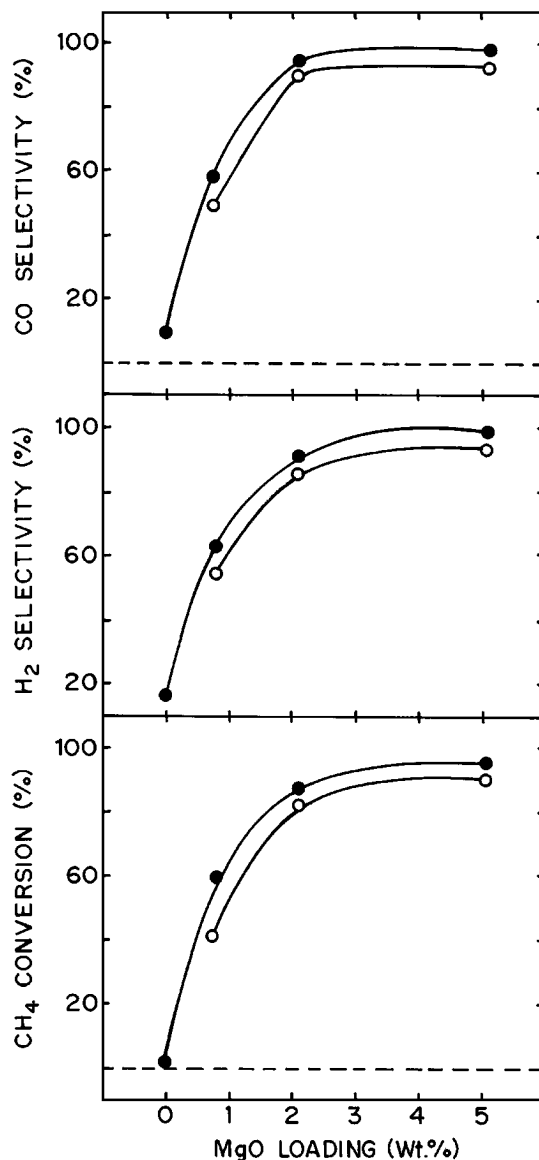


FIG. 3. Variation of the conversion and selectivity in the oxidative methane-to-syngas conversion at 700°C (○) and 800°C (●) with the MgO loading for the NiO (12.2 ± 1.5 wt%)/ $\text{MgO}/\text{SA-5205}$ catalyst [CH_4/O_2 ratio in feed = 1.8, GHSV = $5.2 \times 10^5 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$].

Both the conversion and selectivity of the catalyst are increased sharply with increasing the MgO loading. However, above the MgO loading of about 2 wt%, the influence on the conversion and selectivity is small. For the low MgO loading (2.1 wt%), the TPR curve (Fig. 4B) shows a low temperature reduction peak (between 400 and 500°C), indicating the presence of free-NiO in the catalyst. But the presence of free-NiO is not observed for the catalyst with 5.1 wt% MgO loading (Fig. 4C). A comparison of the TPR curves (Figs. 4A, B, C) clearly shows a sharp decrease in the free-NiO in the catalyst with increasing the MgO loading because of the increased dissolution

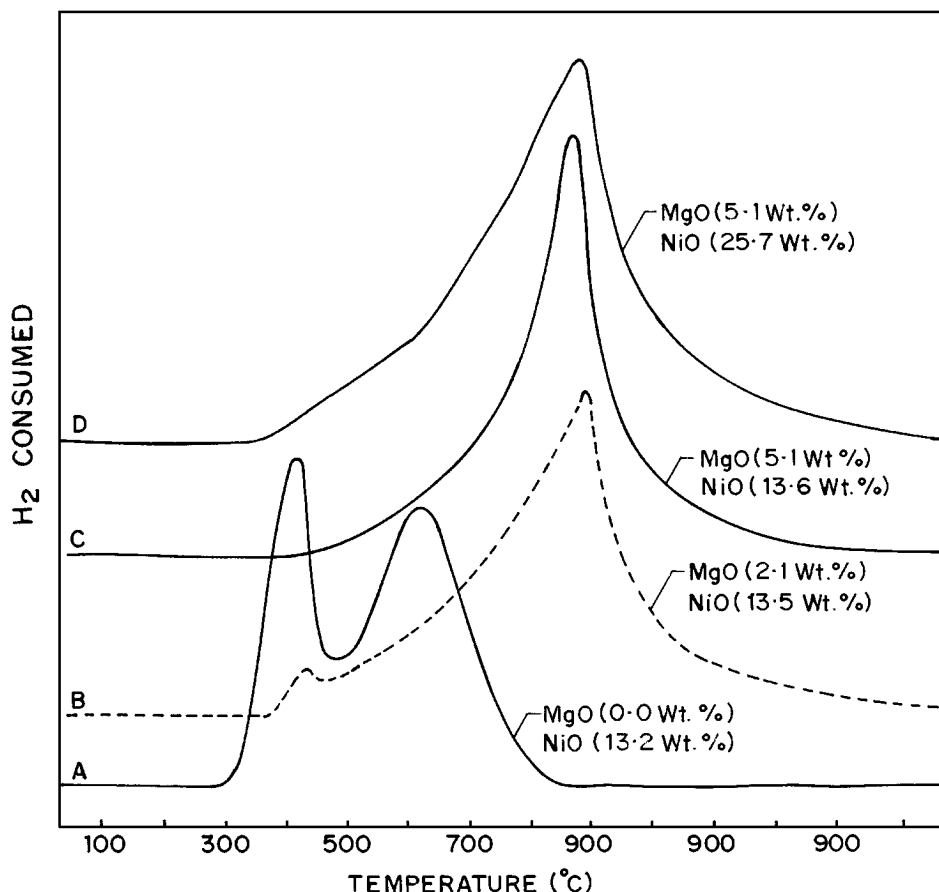


FIG. 4. TPR of nickel oxide supported on catalyst carrier SA-5205 precoated with MgO with different loadings of MgO and NiO.

of NiO in MgO. Consequently, the degree of NiO reduction is also decreased with increasing the MgO loading and the H_2 chemisorption on the reduced catalyst is increased (Table 7).

It may, however, be noted that, when the MgO loading is increased from 2.1 to 5.1 wt%, the change in the NiO reduction is very small but that in the H_2 chemisorption and also in the activity and selectivity is appreciable. This shows that enough MgO on the support is essential for having a perfect NiO-MgO solid solution and also for stabilising nickel in the catalyst against sintering.

Influence of NiO Loading on MgO Precoated Support

Results showing the influence of NiO loading in the NiO/MgO/SA-5205 catalyst, having the same loading of MgO (5.1 wt%), on its performance in the oxidative methane-to-syngas conversion are presented in Fig. 5. TPR curves and the data on the degree of reduction and H_2 chemisorption for the catalyst with different NiO loadings (0–25.5 wt%) are included in Fig. 4 and Table 7, respectively.

The influence of NiO loading as compared to that of MgO loading in the catalyst on the conversion and selec-

tivity is quite small. With the increase in the NiO loading from 1.6 to 25 wt%, the CO selectivity is almost unchanged but the methane conversion and H_2 selectivity are passed through a maximum (at the NiO loading of about 10 wt%).

For the high NiO loading (25.7 wt%), the TPR curve has a hump at low temperatures (350–550°C) and the reduction starts at lower temperatures (at about 350°C), indicating the presence of free-NiO to an appreciable extent. This is consistent with the high degree of NiO reduction as compared to that for the 13.6 wt% NiO loading (Table 7). However, the H_2 chemisorption for the higher NiO loading is smaller. This indicates that, for the higher NiO loading, the sintering of nickel is greater. The observed lower catalytic activity for the catalyst with 25.7 wt% NiO loading is consistent with its lower H_2 chemisorption (Fig. 5 and Table 7).

Influence of Calcination Temperature

The influence of calcination temperature of the NiO (13.6 wt%)/MgO (5.1 wt%)/SA-5205 catalyst on the conversion and selectivity in the catalytic process, TPR, degree of NiO reduction and H_2 chemisorption (after the reduction)

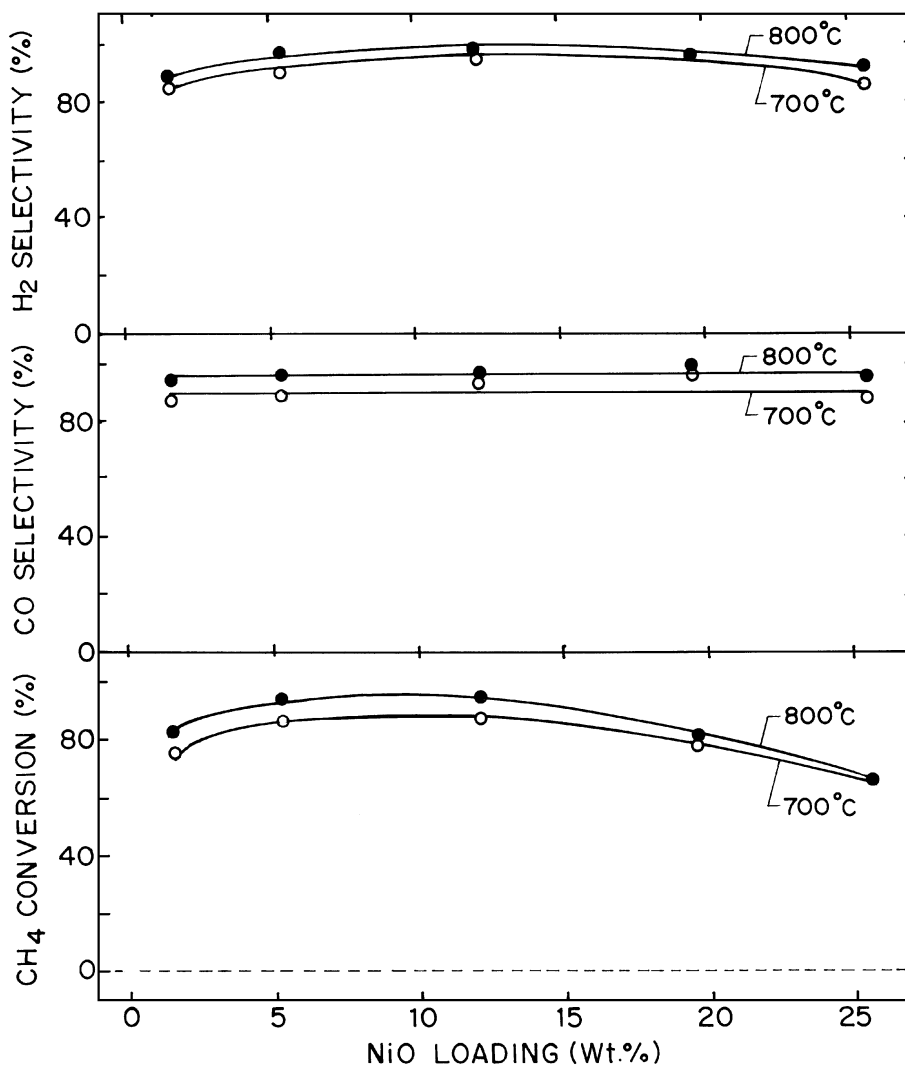


FIG. 5. Variation of the conversion and selectivity in the oxidative methane-to-syngas conversion at 700°C (O) and 800°C (●) with the NiO loading for the NiO/MgO (5.1 wt%)/SA-5205 catalyst [CH_4/O_2 ratio in feed = 1.8, GHSV = $5.2 \times 10^5 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$].

is shown in Figs. 6–8. From the results, the following general observations can be made.

The increase in the catalyst calcination temperature from 600 to 900°C has little or no effect on the conversion and selectivity. But a further increase in the calcination temperature results in a decrease in the conversion; the catalytic activity is totally killed by the calcination at 1200°C.

With the increase in the calcination temperature, the shape of TPR curve is changed, the temperature at which the reduction of the catalyst starts is gradually increased and also the TPR curve and also its peak maximum is gradually shifted towards the higher temperature side (Fig. 7). The degree of NiO reduction is also decreased appreciably (Fig. 8a). These observations suggest that the incorporation of Ni^{2+} in the MgO matrix forming NiO–MgO solid-solution is increased with increasing the temperature because of the higher diffusivity of the ionic Ni^{2+} and O^{2-}

species in solid phase at higher temperature. However, at a very high calcination temperature (1200°C), there is a high possibility of the formation of NiAl_2O_4 (spinel) because of the higher mobility of Ni^{2+} species. Indeed, the presence of NiAl_2O_4 as a major phase in the catalyst calcined at 1200°C is confirmed by XRD. However, at the calcination temperature of 1050°C, the presence of this phase only in traces was observed.

The H_2 chemisorption is decreased with increasing the calcination temperature; the decrease is sharp above 900°C (Fig. 8b). The observed large decrease in the conversion with increasing the calcination temperature, above 900°C is quite consistent with the sharp decrease in the H_2 chemisorption. Thus, influence of the catalyst calcination temperature, particularly above 900°C is attributed to both the sintering of nickel and the strong nickel-support chemical interactions.

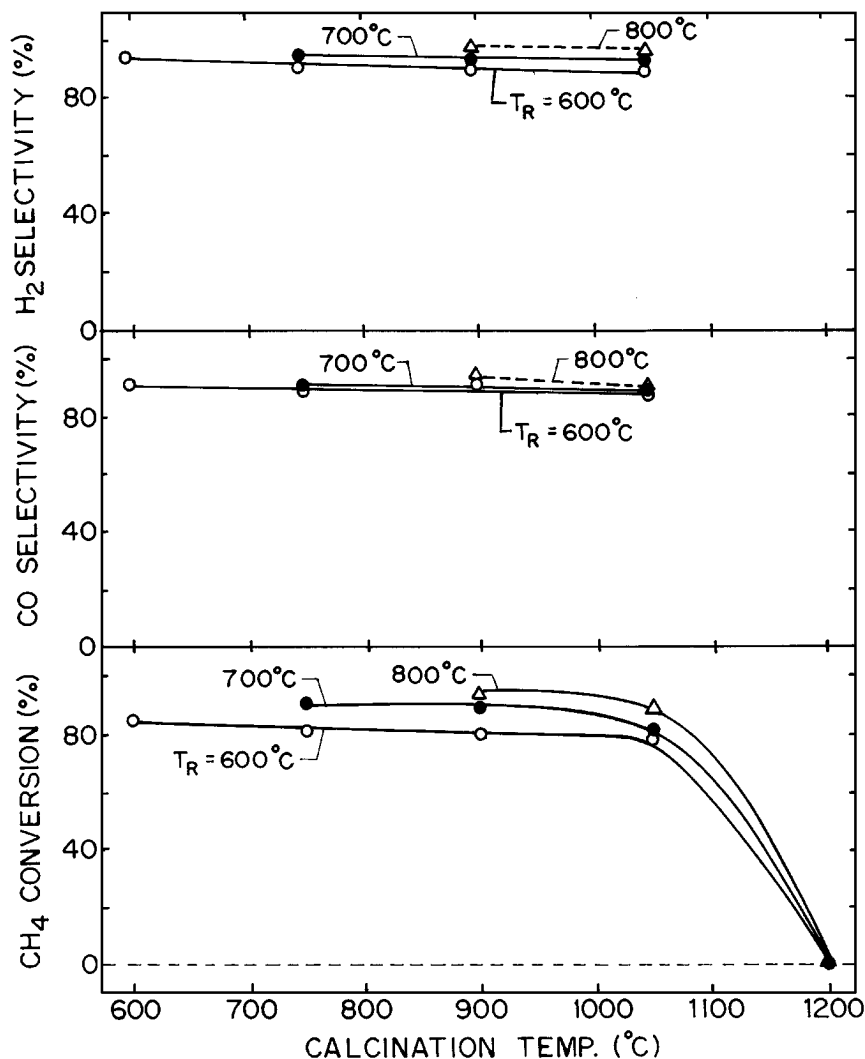


FIG. 6. Dependence of the conversion and selectivity in the oxidative methane-to-syngas conversion over NiO (13.6 wt%)/MgO (5.1 wt%)/SA-5205 catalyst on its calcination temperature [Reaction temperature (T_R): 600°C (O), 700°C (●) and 800°C (Δ); CH_4/O_2 ratio in feed = 1.8, GHSV = $5.2 \times 10^3 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$].

CONCLUSIONS

From the studies on the oxidative conversion of methane to syngas over the supported Ni-catalyst (prepared by different methods and using different commercial low surface area porous catalyst carriers or prepared with different compositions) and their TPR and H_2 chemisorption (after reduction), following important conclusions have been drawn:

1. The conversion and selectivity observed for unsupported NiO-MgO are reduced markedly by depositing it on the catalytic carriers containing Al_2O_3 and SiO_2 at higher concentrations and having higher surface area. However, when the supported catalyst is prepared by depositing NiO on the catalyst carriers precoated with MgO, the influence of support is drastically reduced and the supported catalysts show performance in the catalytic pro-

cess comparable to that of the unsupported NiO-MgO. The supported catalysts prepared using SA-5205 and SZ-5564 supports show even slightly superior performance. For these supported catalysts, the formation of NiO-MgO solid solution, degree of NiO reduction, and H_2 chemisorption are strongly influenced by the different supports used.

2. The conversion and selectivity, TPR, degree of NiO reduction, and H_2 chemisorption (or nickel surface area) of the supported catalyst (NiO/ MO_x /SA-5205, where MO_x is the support precoating agent (viz. MgO, CaO, SrO, BaO, Sm_2O_3 , or Yb_2O_3) are strongly influenced by the precoating agent. The catalyst prepared using SrO or BaO as the support precoating agent shows little or no catalytic activity but that prepared using MgO as the support precoating agent shows highest conversion and selectivity in the process. The catalyst characteristics are strongly influenced by the MgO

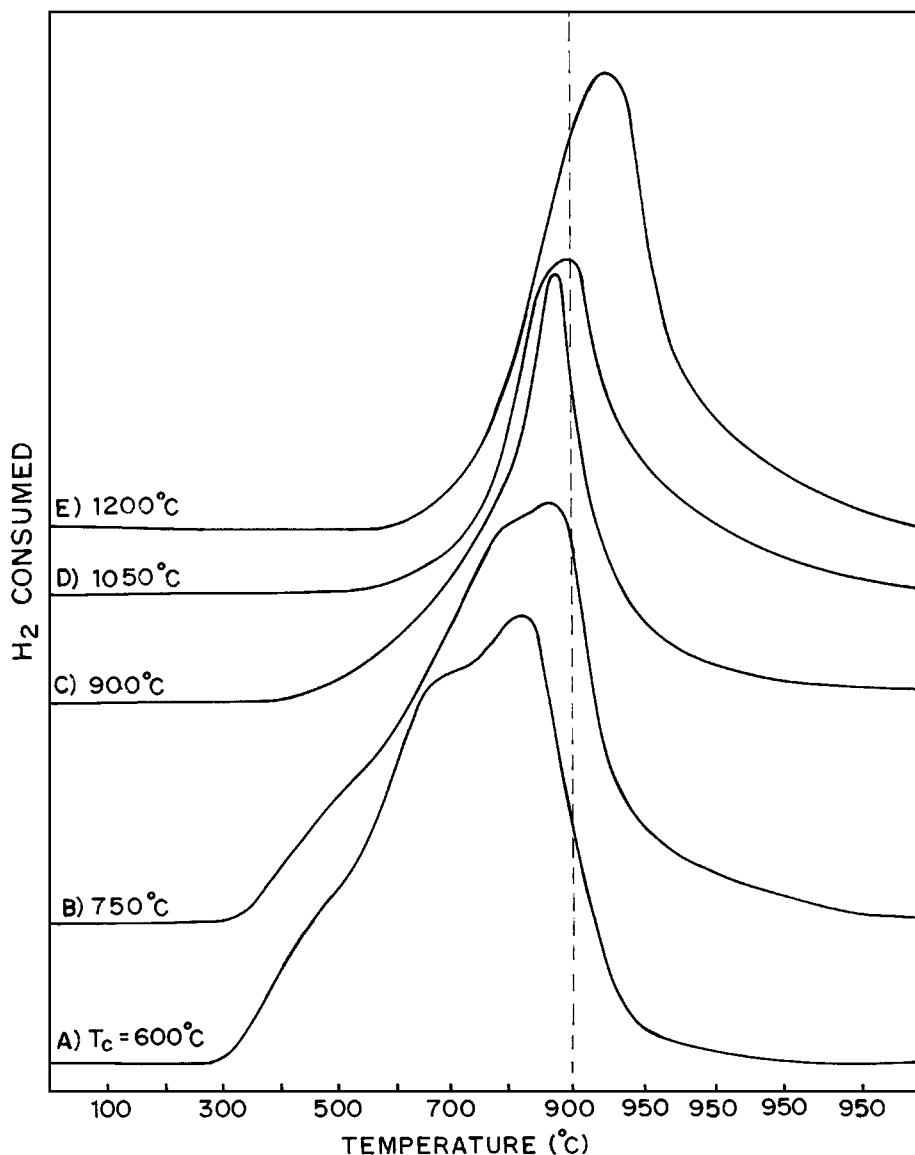


FIG. 7. TPR of NiO/MgO/SA-5205 catalyst calcined in air at different temperatures (loading of MgO and NiO = 5.1 and 13.6 wt%, respectively).

loading, particularly at lower loadings (<2 wt%). However, the influence of NiO loading on the NiO/MgO/SA-5205 catalyst on the conversion/selectivity and other characteristics is relatively much smaller.

3. In the supported Ni-catalysts prepared by depositing NiO on support precoated with MgO, the MgO plays two important roles—one, to avoid the chemical interactions of the catalytically active component (NiO) with the reactive components of support (viz., Al_2O_3 and SiO_2) by providing a stable protective layer of MgAl_2O_4 (spinel) and/or Mg-silicate on the support surface; second, to stabilise nickel on the support surface against sintering by forming a NiO-MgO solid solution.

4. The NiO-MgO solid solution formation and consequently TPR and degree of NiO reduction of the

NiO/MgO/SA-5205 catalyst are strongly influenced by its calcination at different temperatures (600–1200°C). The catalyst calcination upto 900°C has a little or no effect on the conversion/selectivity and a small effect on the H_2 chemisorption but these are drastically reduced when the calcination temperature is increased further, particularly above 1050°C, because of sintering and/or formation of catalytically inactive NiAl_2O_4 .

5. The activity/selectivity of the different supported Ni-catalysts is consistent with their H_2 chemisorption, showing a good correlation between the two.

6. Among the supported Ni-catalysts, NiO/MgO/SA-5205 (loading of NiO and MgO = 13.6 and 5.1 wt%, respectively) showed best performance in the oxidative methane-to-syngas conversion process.

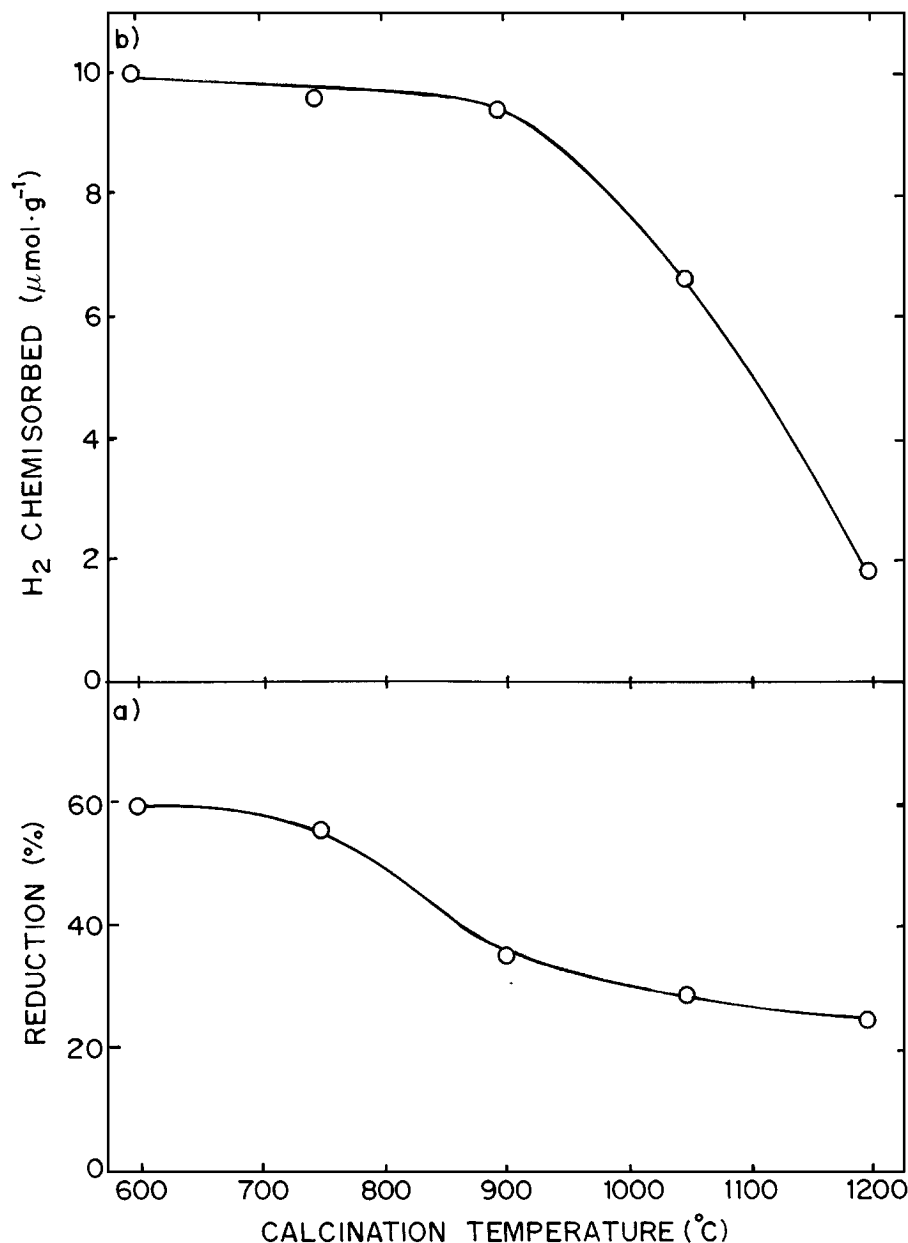


FIG. 8. Effect of calcination temperature of NiO/MgO/SA-5205 catalyst on (a) degree of reduction and (b) H₂ chemisorption on the reduced catalyst (loading of MgO and NiO = 5.1 and 13.6 wt%, respectively).

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REFERENCES

1. Aschroft, A. T., Cheetham, A. K., Foord, J. S., Green, M. L. H., Grey, C. P., Murrel, A. J., and Vernon, P. D. F., *Nature* **344**, 319 (1990).
2. Vernon, P. D. F., Green, M. L. H., Cheetham, A. K., and Aschroft, A. T., *Catal. Lett.* **6**, 181 (1990). [*Nature* **352**, 225 (1991); *Catal. Lett.* **13**, 417 (1992)]
3. Dissanayake, D., Rosynek, M. P., Kharas, K. C. C., and Lunsford, J. H., *J. Catal.* **132**, 117 (1991).
4. Choudhary, V. R., Sansare, S. D., and Mamman, A. S., *Appl. Catal.* **90**, L1 (1992).
5. Choudhary, V. R., Rajput, A. M., and Rane, V. H., *Catal. Lett.* **16**, 269 (1992).
6. Choudhary, V. R., Mamman, A. S., and Sansare, S. D., *Angew. Chem. Int. Ed. Engl.* **31**, 1189 (1992).
7. Choudhary, V. R., Rajput, A. M., and Prabhakar, B., *Catal. Lett.* **15**, 363 (1992).
8. Choudhary, V. R., Rajput, A. M., and Rane, V. H., *J. Phys. Chem.* **96**, 8686 (1992). [*Catal. Lett.* **22**, 289 (1993)]

9. Choudhary, V. R., Rajput, A. M., and Prabhakar, B., *J. Catal.* **139**, 329 (1993).
10. Schmidt, L. D., and Hickman, D. A., *Science* **259**, 343 (1993); *J. Catal.* **138**, 267 (1992).
11. Schmidt, L. D., Haufear, E. A., and Hickman, D. A., *Catal. Lett.* **17**, 223 (1993).
12. Tornianan, P. M., Chu, X., and Schmidt, L. D., *J. Catal.* **146**, 1 (1994).
13. Lapszewicz, J. A., and Jiang, X. Z., *Prepr. Am. Chem. Soc., Div. Petr. Chem.* **37**, 252 (1992).
14. Choudhary, V. R., Uphade, B. S., and Mamman, A. S., *Catal. Lett.* **32**, 387 (1995).
15. Uphade, B. S., Mamman, A. S., and Choudhary, V. R., *Catalysis: Modern Trends* (N. M. Gupta and D. K. Chakraborty, Eds.), p. 380. Narosa, New Delhi, 1995.
16. Highfield, J. G., Bossi, A., and Stone, F. S., *Stud. Surf. Sci. Catal.* **16**, 181 (1983).
17. Paramaliana, A., Arena, A., Frusteri, F., and Giordano, N., *J. Chem. Soc. Faraday Trans.* **86**, 2663 (1990).