

**ENERGY EFFICIENT OXIDATIVE CONVERSION OF
METHANE TO SYNGAS**

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BY

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TO

MY FAMILY

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(Ajit Singh Mamman)

CERTIFICATE AS PER FORM 'A'

Certified that the work incorporated in the thesis "Energy Efficient Oxidative Conversion of Methane to Syngas" submitted by Mr. Ajit Singh Mamman was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.



(Dr. Vasant R. Choudhary)

Research Guide

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SUMMARY AND CONCLUSIONS

Syngas (a mixture of carbon monoxide and hydrogen) is a versatile feedstock for methanol and ammonia syntheses processes and also for a number of Fischer-Tropsch syntheses for the production of liquid fuels, olefins and oxygenates. For the effective utilization of methane/natural gas, syngas-based routes are being considered for converting natural gas into value added and easily transportable products, such as methanol, dimethyl ether, gasoline, middle distillates, etc.

Syngas is produced presently by steam reforming of methane or higher hydrocarbons. However, this process is highly endothermic and hence, highly energy intensive and more over produces syngas with high H₂/CO ratio (> 4.0) due to the side water gas reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) and thereby producing low selectivity and yield for carbon monoxide. Because of the above limitations of the steam reforming process, worldwide efforts have been made during the last 7-8 years for developing a new process for producing CO and H₂ by catalytic partial oxidation of methane using different nickel and noble metal containing catalysts, CO₂ reforming of methane, simultaneous steam and CO₂ reforming of methane, and also by simultaneous oxidative conversion and steam and/or CO₂ reforming of methane involving a coupling of exothermic and endothermic reactions. The present work, for the Ph.D. thesis was, therefore undertaken as a part of the comprehensive research program in our laboratory for the systematic development of the highly active, selective and productive catalysts and the underlying processes for the catalytic conversion of methane into syngas in an energy efficient and safe manner, with the following objectives.

The Ph.d. thesis has been divided into the following four parts.

PART I: LITERATURE SURVEY, OBJECTIVES AND SCOPE

In this part, the literature survey on the above methane-to-syngas conversion reactions and objectives/scope of the work have been given.

PART II: EXPERIMENTAL

In this part, the experimental methods and surface characterization techniques in the present work has been discussed.

PART III: CATALYTIC PARTIAL OXIDATION OF METHANE TO SYNGAS

In this part, the work on the oxidative conversion of methane to syngas over a number of Ni, Co and/or noble metal containing catalysts has been presented.

CHAPTER 3.1: NiO-ALKALINE EARTH OXIDE(S) CATALYSTS FOR OXIDATIVE METHANE-TO-SYNGAS CONVERSION : INFLUENCE OF ALKALINE EARTH OXIDE ON THE SURFACE PROPERTIES AND TEMPERATURE PROGRAMMED REDUCTION/REACTION BY H₂ AND METHANE

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 4h) has been studied. Temperature programmed reduction of these catalysts and NiO-MgO with different Ni/Mg ratios by H₂ 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 H₂ at a very low contact time (1ms). 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 H₂ 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.

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.

- The surface area, reduction by H₂ or reducibility of NiO, surface composition of nickel relative to that of alkaline earth(s) before and after the reduction by H₂ 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.

- The catalyst sintering is increased because of the addition of higher alkaline earth oxide(s) to NiO.
- The reducibility by H₂ 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)].
- 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).
- The surface Ni/alkaline earth(s) ratio for all the catalysts is decreased due to their reduction by H₂; 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.
- 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.

CHAPTER 3.2: OXIDATIVE CONVERSION OF METHANE TO SYNGAS OVER NiO-MgO SOLID SOLUTIONS WITH OR WITHOUT CONTAINING COBALT

Performance of NiO-MgO with different Ni/Mg ratios (0.02 to 10.0) calcined at different temperature (750-1200°C) and with or without reduction by H₂ at different temperature (500-900°C) and also of Co/MgO (0 - ∞) and Ni : Co : MgO = 0.5 : 0.5 : 1.0) in the oxidative conversion of methane to syngas at different process conditions has been carried out.

CONCLUSIONS

From this investigation, the following important conclusions can be drawn.

- NiO-MgO (Ni/Mg = 1.0-3.0) is a highly promising catalyst for the oxidative conversion of methane to syngas at a very low contact time. It shows high activity and selectivity for both CO and H₂, high stability (or long life) and also very high productivity in the process at a very high space velocity (5.0 x 10⁵ cm³ g⁻¹ h⁻¹).

- The prereduction by H₂ at different temperatures (500-900°C) has only a little effect on the catalytic activity of the NiO-MgO catalyst. The catalyst temperature has also only a small effect on the performance of the NiO-MgO catalyst.
- The performance of the CoO-MgO catalyst is inferior to NiO-CoO-MgO and NiO-MgO catalysts. The replacement of half of the NiO from the NiO-MgO catalysts by CoO has little or no effect on the conversion and selectivity in the process.

CHAPTER 3.3: OXIDATIVE CONVERSION OF METHANE TO SYNGAS OVER Ru - OR Pt-CONTAINING NiO-MgO SOLID SOLUTIONS

Partial oxidation of methane to syngas (CO and H₂) over Ru or Pt (1.0 wt%) NiO-MgO (3.0) catalyst, with or without its prereduction by H₂ (at 500°C for 1h), has been investigated at different temperatures (500°-800°C) at a very low contact time (space velocity : $5.1 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$). The prereduction of both Pt-or Ru-containing catalysts has an advantageous effect; Both the conversion and selectivity for CO and H₂ are increased due to the prereduction. The addition of Pt or Ru to NiO-MgO solid solution results in an increase in both the conversion and selectivity. The observed beneficial effects of the of Ru or Pt and prereduction by H₂ are attributed to an increase in reduction of NiO from the NiO-MgO solid solution due to the spillover of H-atoms from noble metals to the NiO buried in the MgO matrix of the NiO-MgO solid solution. The increase in NiO reduction was confirmed by the temperature programmed reduction (TPR) of the catalysts by H₂ (2.0 mol% H₂ in Ar) from 50° to 900°C. The degree of NiO reduction of NiO-MgO, Pt/NiO -MgO and Ru/NiO-MgO catalysts in their TPR was found to be 11.5, 24.7 and 26.3%, respectively.

CONCLUSIONS

Following important conclusions can be drawn from the TPR and the oxidative methane-to-syngas conversion over the NiO-MgO solid solution with or without containing Pt (1.0 wt%) or Ru (1.0 wt%).

- The amount of hydrogen consumed and consequently the degree of reduction of NiO from the NiO-MgO catalyst are increased because of the addition of Pt or Ru to the catalyst. The increase in the degree of reduction of the catalyst is attributed mainly to the spillover of hydrogen (highly active atomic hydrogen) on the noble metal.

- Both the catalytic activity and selectivity (in the oxidative methane-to-syngas process) of the NiO-MgO solid solution are increased appreciably because of the addition of the Pt or Ru to the solid solution.
- The prereduction by the hydrogen (at 500°C) of the Pt or Ru/NiO-MgO catalysts is beneficial for the oxidative conversion of methane to syngas; both the conversion and selectivity are increased due to the prereduction.

CHAPTER 3.4: OXIDATIVE CONVERSION OF METHANE TO CO AND H₂ OVER Pt-OR Pd-CONTAINING ALKALINE AND RARE EARTH OXIDE CATALYSTS

A number of Pt (1.0 wt %) and Pd (1.0 wt%) containing alkaline earth oxide (viz. MgO and CaO) and rare earth oxide (viz. La₂O₃, Pr₆O₁₁, Nd₂O₃, Sm₂O₃, Gd₂O₃, Dy₂O₃ and Er₂O₃) catalysts have been compared for their performance in the oxidative conversion of methane to CO and H₂ at 700° and 800°C and at very low contact time [GHSV= 5.0 (± 0.2) × 10⁵ cm³ g⁻¹ h⁻¹]. The catalysts are characterized for their specific surface area and H₂ chemisorption at 40°C. Among the Pt and Pd containing catalysts, the best performance is shown by Pt/ Gd₂O₃ and Pd/Sm₂O₃, respectively. These catalysts show high selectivity for CO but low selectivity for hydrogen due to reverse water gas shift reaction. Since alkaline and rare earth oxides are basic in nature, they act not only as a support for dispersing noble metals but also play significant role in deciding the activity/ selectivity of the Pt- or Pd- containing catalysts.

CONCLUSIONS

The Pt/Gd₂O₃, Pt/MgO and Pd/Sm₂O₃ catalysts show activity and high selectivity and also high productivity for CO but low selectivity for H₂, due to the reverse water gas shift reaction, in the oxidative conversion of methane to CO and H₂ at very low contact time. In general, the activity/selectivity of Pt containing alkaline and rare earth oxide catalysts is higher than the Pd containing catalysts. There is, however, no direct correlation between the H₂ chemisorption (or dispersion of the noble metals) on the Pt or Pd catalysts and their activity/selectivity in the process. The alkaline earth and rare earth oxides are basic in nature and therefore act not only as support for dispersing the noble metals but also play significant role in deciding the activity and selectivity of the Pt or Pd containing alkaline earth and rare earth oxide catalysts in the catalytic process.

CHAPTER 3.5: PARTIAL OXIDATION OF METHANE TO CO AND H₂ OVER COBALT CONTAINING ZrO₂, ThO₂, UO₂, TiO₂ AND SiO₂ CATALYSTS

Influence of different metal oxide supports (viz. ZrO₂, ThO₂, UO₂, TiO₂, and SiO₂) on the performance of Ni and/or Co containing catalysts [Ni and/or Co/MO₂ mole ratio (where M = Zr, Th, U, Ti, or Si) = 1.0] in the oxidative methane-to-syngas conversion at very low contact time (GHSV = 5.2 x 10⁵ cm³.g⁻¹.h⁻¹ at STP) has been investigated. The nickel containing ZrO₂, ThO₂ and UO₂ catalysts (with or without prereduction by hydrogen at 500°C) showed good performance in the process; the order of their performance is NiO-ThO₂>NiO-UO₂>NiO-ZrO₂. The NiO-TiO₂ showed appreciable catalytic activity only after its reduction at 800°C. However, this catalyst and the NiO-SiO₂ catalyst showed poor performance in the process. These two catalysts are also deactivated very fast, mostly due to sintering of Ni and/or formation of catalytically inactive binary metal oxide phases by solid-solid reaction at the high catalyst calcination and/or catalytic reaction temperature. Although, the Ni-containing ThO₂, UO₂ and ZrO₂ catalysts showed good performance, the carbon deposition on them during the process is fast. However, because of the addition of cobalt to these catalysts (with Co/Ni = 1.0), the rate of carbon deposition on them in the process is drastically reduced. But, the Co addition resulted in a significant decrease in both the conversion and selectivity; the decrease in the selectivity was small.

The studies on the influence of time-on-stream, space velocity, CH₄/O₂ feed ratio, catalyst dilution and catalyst particle size on the conversion and selectivity at different temperatures in the oxidative conversion of methane to syngas over the NiO/MgO/SA-5205 catalyst lead to the following important

CONCLUSIONS

NiO-ThO₂ catalyst with or without reduction by H₂ shows very high activity/selectivity for both H₂ and CO in the oxidative conversion of methane to syngas at extremely low contact time (GHSV = 5.2 x 10⁵ cm³ g⁻¹ h⁻¹ at STP). The NiO-ZrO₂ and NiO-UO₂ catalysts also show good performance. The carbon deposition on these catalysts in the process is drastically reduced because of the addition cobalt to them. However, the cobalt addition results in small decrease in both catalytic activity and selectivity of these catalysts. The NiO-TiO₂ and NiO-SiO₂ catalysts show poor activity and selectivity in the process and deactivated very fast, probably due to strong metal (Ni)-support (TiO₂ or SiO₂) physico-chemical interactions at the high reaction

temperature.

CHAPTER 3.6: OXIATIVE CONVERSION OF METHANE TO SYNGAS OVER NiO/MgO SOLID SOLUTION SUPPORTED ON LOW SURFACE AREA CATALYST CARRIER

● Influence of time-on-stream (0.5-15h), CH₄/O₂ ratio in feed (1.8-8.0), space velocity (6000-5,10,000 cm³ g⁻¹ h⁻¹), catalyst particle size (22-70 mesh), catalyst dilution by inert solid particles (diluent/catalyst weight ratio = 4) on the performance at different temperatures (600°-900°C) of the NiO/MgO solid solution deposited on SA-5205 [which is a low surface area macroporous silica-alumina catalyst carrier] in the oxidative conversion of methane to syngas (a mixture of CO and H₂) has been investigated. The conversion and H₂ selectivity are increased at 700°C to a small extent and leveled-off during the short initial reaction period of about 1h. The dependence of conversion and selectivity in the process on the space velocity is strongly influenced by the temperature. Both the conversion and selectivity for H₂ and CO are decreased markedly with increasing the CH₄/O₂ ratio in the feed. The catalyst dilution resulted in a small but significant decrease in both the conversion and selectivity for H₂ and CO. The increase in the catalyst particle size had also a small but significant effect on both the conversion and selectivity in the oxidative conversion process. Both the heat and mass transfer processes seem to play significant role in the oxidative conversion of methane to syngas at a very low contact time or very high space velocity (5.1 x 10⁵ cm³ g⁻¹ h⁻¹).

CONCLUSIONS

- The catalyst shows no sign of deactivation when on the time-on-stream for 15h.
- The effect of space velocity on the conversion and selectivity is small and, moreover, depends on the reaction temperature.
- Both the conversion and selectivity are decreased with increasing the CH₄/O₂ ratio in the feed.
- Because of the catalyst dilution by inert solid particles, both the conversion and selectivity are decreased.
- The conversion and selectivity are increased to a small extent with increasing catalyst particle size

- The observed effects of the space velocity, CH₄/O₂ feed ratio, catalyst dilution and catalyst particle size indicate that the catalytic reaction is influenced by both the heat and mass transfer processes, particularly at the lower temperatures.

PART IV CATALYTIC STEAM AND /REFORMING WITH OR WITHOUT SIMULTANEOUS OXIDATIVE CONVERSION OF METHANE TO SYNGAS

CHAPTER 4.1: CO₂ REFORMING, SIMULTANEOUS CO₂ AND STEAM REFORMING AND OXY-CO₂ OR STEAM REFORMING OF METHANE OVER NiO-MgO SOLID SOLUTION

Methane-to-CO and H₂ conversion reactions, involving CO₂ reforming, simultaneous steam and CO₂ reforming and oxy-steam reforming and CO₂ reforming oxy-CO₂ reforming, CO₂ reforming, simultaneous steam and CO₂ reforming, over NiO-MgO solid solution (Ni/Mg = 0.5) have been investigated. The catalyst shows high activity and selectivity in the oxy-steam reforming and oxy-CO₂ reforming reactions, at 800°-850°C and high space velocity [(40-50) x 10³ cm³ g⁻¹ h⁻¹]. These two processes involve coupling of the exothermic oxidative conversion and endothermic steam or CO₂ reforming reactions, making both the processes highly energy efficient and also safe to operate. The catalyst also shows high methane conversion activity (nearly 95% conversion) with 100% selectivity for both CO and H₂ in the simultaneous steam and CO₂ reforming of methane at (800°-850°C) at high space velocity (3.6 x 10³ cm³ g⁻¹ h⁻¹).

CONCLUSIONS

The NiO-MgO solid solution shows high catalytic activity and selectivity not only in the oxidative conversion of methane to syngas but also in the oxy-CO₂ reforming and oxy-steam reforming, CO₂ reforming and simultaneous CO₂ and steam reforming of methane to syngas. In the oxy-steam and oxy-CO₂ reforming processes, the exothermic oxidative conversion and endothermic steam or CO₂ reforming reactions are coupled, making the process highly energy efficient and also safe to operate.

CHAPTER 4.2: CO₂ REFORMING, OXY-CO₂ REFORMING AND OXY-STEAM REFORMING OF METHANE TO SYNGAS OVER NiO-CoO-MgO SOLID SOLUTION

CO₂ reforming, oxidative conversion and simultaneous oxidative conversion and CO₂ or steam reforming of methane to syngas (CO and H₂) over NiO-CoO-MgO (Co: Ni : Mg = 0.5 : 0.5 : 1.0) solid solution at 700°-850°C and high space velocity ($5.1 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$ for oxidative conversion and $4.5 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$ for oxy-steam or oxy-CO₂ reforming) for different CH₄/O₂ (1.8-8.0) and CH₄/CO₂ or H₂O (1.5-8.4) ratios have been thoroughly investigated. Because of the replacement of 50 mol% of the NiO by CoO in NiO-MgO (Ni/Mg = 1.0), the performance of the catalyst in the methane to syngas conversion process is improved; the carbon formation on the catalyst is drastically reduced. The CoO-NiO-MgO catalyst shows high methane conversion activity (methane conversion > 80%) and high selectivity for both CO and H₂ in the oxy-CO₂ reforming and oxy-steam reforming processes at $\geq 800^\circ\text{C}$. The oxy-steam or CO₂ reforming process involves the coupling of the exothermic oxidative conversion and endothermic CO₂ or steam reforming reactions, making these processes highly energy efficient and also safe to operate. These processes can be made thermoneutral or mildly exothermic or mildly endothermic by manipulating the process conditions (viz., temperature and/or CH₄/O₂ ratio in the feed).

CONCLUSIONS

The NiO-CoO-MgO catalyst shows high activity and selectivity in the conversion of methane to syngas by the oxidative conversion, CO₂ reforming, oxy-CO₂ reforming and oxy-steam reforming reactions. The addition of CoO to NiO-MgO catalyst has beneficial effect on the process performance for eliminating or drastically reducing the formation of filamental carbon on the catalyst particularly in the process involving the CO₂ reforming of methane. In the oxy-CO₂ and oxy-steam reforming processes over this catalyst, the exothermic oxidative conversion and endothermic CO₂ or steam reforming reactions are coupled, making these processes highly energy efficient and non-hazardous or safe to operate.

CHAPTER 4.3: CO₂ REFORMING, STEAM REFORMING AND SIMULTANEOUS CO₂ AND STEAM REFORMING OF METHANE OVER Co_xNi_{1-x}O SUPPORTED ON MACROPOROUS SILICA ALUMINA PRECOATED WITH MgO

Conversion of methane to CO and H₂ by CO₂ reforming, steam reforming and by both the reactions occurring simultaneously over Co_xNi_{1-x}O (x = 0.0-0.5) supported on commercial macroporous silica-alumina catalyst carrier (SA-5205, obtained from M/S Norton Co. U.S.A.)

precoated with MgO at different temperatures (700°-900°C) and contact times (0.025-0.29 s at STP) has been investigated. With the increasing Co/Ni ratio of the catalyst, its surface area is decreased and its degree of reduction in TPR (by H₂) from 100° to 900°C is increased. The influence of Co/Ni ratio of the catalyst and feed ratios (H₂O/CH₄ = 0.4 - 4.0 and CO₂/CH₄ = 0.3 - 1.2) on the conversion and selectivity or H₂/CO product ratio has also been thoroughly investigated. With the increase of the Co/Ni ratio, the methane conversion and CO selectivity in the steam reforming is decreased, the carbon deposition on the catalyst during the CO₂ reforming is reduced drastically and the conversion of methane and CO₂, H₂ selectivity and H₂/CO ratio in the CO₂ reforming is passed through a maximum and also the conversion, particularly of methane, in the simultaneous steam and CO₂ reforming is passed through a maximum, at the Co/Ni ratio of about 0.17. The supported catalyst with Co/Ni ratio of 0.17 shows high methane conversion activity (methane conversion > 95%) and 100% selectivity for both CO and H₂ with H₂/CO ratio varying from 1.2 - 2.2 in the simultaneous steam and CO₂ reforming processes at high and space velocity (24,740 cm³ g⁻¹ h⁻¹). The H₂/CO ratio can be controlled by manipulating the H₂O/CO₂ ratio in the feed, it is increased with increasing the H₂O/CO₂ ratio and vice versa.

CONCLUSIONS

From this investigation, following important conclusions have been drawn.

- The surface and reduction properties, filamental carbon formation in the CO₂ reforming of methane, and methane-to-syngas conversion activity (in the steam and/or CO₂ reforming of methane) over the Co_xNi_{1-x}O/MgO/SA-5205 catalyst (x = 0-0.5) are strongly influenced by the Co/Ni ratio in the catalyst.
- Because of the increase in the Co/Ni ratio, the surface area of the catalyst is decreased, but its degree of reduction is increased.
- The presence of cobalt in the catalyst has a beneficial effect on the formation of filament carbon; the carbon formation is drastically reduced with increasing the Co/Ni ratio in the catalyst. (It is reduced in the CO₂ reforming of methane).
- The presence of cobalt in the catalyst at an optimum Co/Ni ratio (0.17) has also a beneficial effect on the methane-to-H₂ and CO conversion activity in the CO₂ reforming

and simultaneous CO₂ and steam reforming processes. However, in the steam reforming process, it has an adverse effect on the both activity and selectivity of the catalyst.

- The catalyst with the optimum Co/Ni ratio is highly promising catalyst for the conversion of methane to CO and H₂, particularly by the simultaneous CO₂ and steam reforming process.

CHAPTER 4.4: OXY-CO₂ REFORMING, OXY-STEAM REFORMING AND OXY-CO₂ AND STEAM REFORMING OF METHANE OVER CO_xNI_{1-x}O SUPPORTED ON MACROPOROUS SILICA-ALUMINA PRECOATED WITH MgO

Simultaneous oxidative conversion and CO₂ and/or steam reforming of methane, involving coupling of exothermic and endothermic methane-to-syngas conversion reactions, over Co_xNi_{1-x}O (14 ± 0.5 wt%)/MgO (5.1 wt%) /SA-5205 (x = 0.0 - 0.5) catalysts has been thoroughly investigated. Effect of Co/Ni ratio of the catalyst on its performance in the oxy-CO₂, oxy-steam and simultaneous oxy-CO₂ and steam reforming processes has been studied. Influence of the reaction temperature (750°-850°C), space velocity (25000-100,000 cm³ g⁻¹ h⁻¹) and CH₄/O₂, CH₄/CO₂, CH₄/H₂O and CO₂/H₂O feed ratios on the conversion, selectivity, H₂/CO product ratio and net heat of reaction (ΔH_r) in these processes over the catalyst having optimum Co/Ni ratio (0.17) the oxy-CO₂ and oxy-steam reforming processes has also been investigated. The influence of Co/Ni ratio of the catalyst on its performance depends on the process and process conditions. For the oxy-CO₂ and oxy-steam reforming processes, the Co/Ni ratio has a strong influence on the conversion of methane and CO₂ or steam and also on the selectivity for both H₂ and CO. However, for the oxy-CO₂-steam reforming process, Co/Ni ratio has a strong influence on the conversion of CO₂ and H₂O but a little or no influence on the methane conversion and the H₂/CO ratio and hence, for this process, the catalyst with Ni/CO ratio (1.0), which has lower activity for filament carbon formation, is more preferable. In the latter process (at 850°C), the catalyst (with Co/Ni =1.0) shows very high methane conversion activity (97% conversion) and 100% selectivity (based on methane) for both CO and H₂ at a low contact time (15 ms), the H₂/CO ratio can be controlled by manipulating the CO₂/H₂O feed ratio in the process. In all the oxy-CO₂, oxy-steam and oxy-CO₂-steam reforming processes, the exothermic oxidative conversion and endothermic CO₂ and/or steam reforming reactions over the catalyst occur in the same reactor, involving the coupling of the exothermic and endothermic reactions.

Because of the coupling of exothermic and endothermic reactions, these processes are highly energy efficient and also nonhazardous or safe to operate. Moreover, by manipulating the process conditions [viz., temperature and CH_4/O_2 or $\text{CH}_4/(\text{H}_2\text{O}$ and/or $\text{CO}_2)$ feed ratio], these processes can be made mildly endothermic, thermoneutral or mildly exothermic.

CONCLUSIONS

From the studies on the oxy- CO_2 and/or steam reforming processes over the $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{MgO}/\text{SA-5205}$ catalysts ($x = 0.0 - 0.5$) at different process conditions, following important conclusions have been drawn.

- Because of the addition of cobalt to the catalyst, in addition to having a better stability against filamental carbon formation, the catalyst showed improved performance in the oxy- CO_2 reforming and oxy-steam reforming processes; the optimum Co/Ni ratio in the catalyst for its best performance in these processes is 0.17.
- In case of the simultaneous oxy- CO_2 and steam reforming process, the methane conversion and H_2/CO product ratio is not influenced significantly by the addition of cobalt to the catalyst. Hence, for this process, the catalyst with higher Co/Ni ratio (which has higher stability against filamental carbon formation) is more preferable and it is a highly promising catalyst for this process.
- In the oxy- CO_2 and/or steam reforming processes over the catalyst (with Co/Ni ratio of 0.17 and 1.0), methane can be converted to CO and H_2 with high conversion (above 95%) and high selectivity (even 100%), depending upon the process) at low contact time or high space velocity ($5 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$).
- In the oxy- CO_2 and/or steam reforming processes, the H_2/CO product ratio can be varied and a desired H_2/CO product ratio can be obtained by manipulating the process conditions, particularly the feed compositions (i.e. relative concentrations of CH_4 , O_2 , CO_2 and /or steam in the feed). Any of these processes can be made mildly exothermic, thermoneutral or mildly endothermic by manipulating the process conditions (particularly, the temperature and CH_4/O_2 ratio in the feed).

PART-I

INTRODUCTION-OBJECTIVES AND SCOPE

1.1. CONVERSION OF METHANE TO SYNGAS – LITERATURE SURVEY

Increasing concern about world dependence upon petroleum oil, in the light of its fast depleting reserves, has provoked increased interest in the efficient utilization of natural gas. Methane, a major constituent of natural gas may be converted to synthesis gas. It is a mixture of carbon monoxide and hydrogen, a highly versatile feedstock, used in methanol, Fischer-Tropsch synthesis processes, carbonylation, hydrogenation, hydroformylation and other industrially important reactions. Almost all options for natural gas/methane utilization involve its initial conversion to synthesis gas. The present section focuses on the industrial importance of synthesis gas and its diverse applications in synthesis of chemicals and liquid fuels and the literature on the conversion of methane to syngas.

Syngas, the technical jargon for mixtures of hydrogen and carbon oxides, is crucially important building block of the chemical industry and is widely used in a variety of processes. Currently, the production of H_2 and CO, synthesis gas, (syngas), is carried out by steam reforming of methane (1,2) partial oxidation of fuel oil (3) coal gasification(4,5) and naphtha reforming (6). Synthesis gas is widely used and can be converted into petrochemicals, higher alcohols, and synthetic fuels. Hydrogen is used in ammonia synthesis and petroleum refining industries, while carbon monoxide is widely used in the production of plastics, paints, foams, pesticides, and insecticides.

Common names of mixtures of CO and H_2 are derived from their origin such as: “water gas” ($CO+H_2O$) from steam gasification of coal and “crack gas”($CO+3H_2O$) from the steam reforming of methane, or from their application such as “methanol synthesis gas” ($CO+2H_2$) for the manufacture of methanol and “oxo gas” ($CO+H_2$) for hydroformylation reactions. Another synthesis gas is ammonia synthesis gas (N_2+3H_2) which does not contain CO as a higher constituent.

Recent focus of syngas conversion development is on catalyst to improve the economics of producing hydrocarbon and/or oxygenate liquid fuels, particularly those suitable for transportation.

The pathways for syngas conversion are:

TH-1239

Table 1.1.1.Syngas Stoichiometry required for some Industrially Important Processes

Process	H ₂ /CO ratio	H ₂ /2(CO+3CO ₂)	Syngas production process	Feedstock
Methanol	≥ 2.0	≥ 1.0	[a] [b] [c]	Natural gas
Methanol-higher alcohols	1.0-2.5	—	[b] [c] (removal of CO ₂) [d] [f] and/or H ₂ in some cases	Natural gas Heavy residue coal, Biomass
Glycol (direct-indirect synthesis)	1.5-1	—	[d] [f] (or [b] with H ₂ partially removed)	Heavy residue coal, Biomass Natural gas
Hydrocarbonylation	1.0	(aldehyde)	[d] [f]	Heavy residue coal, Biomass
	2.0	(alcohol)	[b] (or [c] with H ₂ partial removal)	Natural gas (Steam reforming and Autothermal reforming)
Carbonylation (acetic acid, acetic-anhydride)	0.0	(pure CO)	[a],[b],[c],[d], [e], [f] (selective CO extraction)	Natural gas Heavy residue coal, Biomass
Oxosynthesis	1.0	—	[f]	Coal, Biomass

[a] Steam reforming [c] Steam reforming & Autothermal reforming

[b] Partial oxidation [d] Partial oxidation [e] Gassification

1. Fuels and chemicals by direct synthesis (methanol, ammonia, gasoline, diesel fuel, olefins, and methane).
2. Fuels and chemicals by indirect synthesis via methanol (acetic acid, acetic anhydride, gasoline diesel fuel, ethanol etc.).
3. Chemicals by secondary reactions of products obtained from direct or indirect synthesis (acids, alcohols, single cell protein, etc).

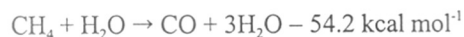
Thus, a remarkable diversity of chemicals/liquid fuels (7) can be synthesized from syngas.

There are several catalytic options available for the production of synthesis gas from natural gas/methane. In addition to the conventional technologies, the main emphasis has been laid on new direct catalytic alternatives in natural gas/methane conversion into synthesis gas. In the present section, new emerging catalytic routes and the conventional technologies available for the generation of synthesis gas from natural gas/methane have been discussed briefly.

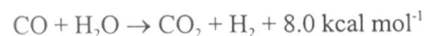
1.1.1. Steam Reforming of Methane [SRM] to Syngas

Steam reforming is the established process for converting methane or natural gas and other hydrocarbons into syngas (1,2). It has been used for several decades since its first development in 1926 (8) and over the years substantial improvements have been introduced. The traditional SRM process consists of feed gas preheating and pretreatment, reforming, high and low shift, CO₂ removal and methanation. Methane is reacted with steam on a Ni-based catalyst in a primary to produce H₂ and CO at residence of several seconds. The catalytic reactions are as follows,

Main reaction



Side reaction



Reformed gas is formed at ca.1200K and pressures of 5-30 bar. Excess of steam is introduced to avoid carbon deposition and the feed H₂O/CH₄ mole ratios are typically 2-5, depending on the syngas end use alkali (K) or alkaline earths (Mg, Ca) are usually introduced in catalyst formulations as to accelerate carbon removal from the catalyst surface. The CH₄ conversion at the exit is typically 90-92% and mixture composition at the exit of the primary reformer approaches that predicted by thermodynamic equilibrium for a CH₄:H₂O ratio = 1: 3 feed.

A secondary reformer is placed just at the exit of the primary reformer in which the unconverted methane is reacted with O_2 at the top of the refractory lined tube. The mixture is then equilibrated on a Ni catalyst located below the oxidation zone. For the production of hydrogen for ammonia synthesis (H_2/N_2), CO contained in the reformer effluents is converted to additional hydrogen in high and temperature shift converters.

For methanol plants, a high temperature shift (HTS) on Fe_2O_3/Cr_2O_3 catalyst at $400^\circ C$ is followed by a low temperature shift (LTS) reactor at $200^\circ C$ on a Cu/ZnO catalyst. For ammonia synthesis plants only the HTS reactor is used. The CO_2 produced in reformers and shift converters is removed from the process gas by chemical absorption processes, such as monoethanol amine (MEA) or hot K_2CO_3 . The level of carbon oxides still remaining in H_2 stream leaving the CO_2 removal absorber is reduced to a minimum by methanation. The methanation reaction is the reverse of the steam reforming reaction and typically takes place at $250-290^\circ C$. This traditional process produces H_2 at a purity of 95 to 98% with impurity being predominantly methane.

The steam reforming of methane has been documented extensively in the literature. A general description of steam reforming was given by Bridger (8, 9) Rostrup - Nielsen (10) and Jockel (11), where as reviews by Ross (2) Trimm (13), van Hook (14) and Bortholomew (15) have dealt with specific catalytic problems. Rostrup-Nielsen (16) discusses both the catalytic chemistry of steam reforming and the way in which it is interrelated with reactor and plant design.

The influence of catalyst formulations and structure on catalyst behavior (activity, stability, etc.) is described by Ross(12) and made extensive reference to Rostrup-Nielsen's work, the results of which has now been compiled together (10).

Today, steam reforming is a principal process for the production of H_2 and synthesis gas. More than 80% of world ammonia production is based on steam reforming. Though, steam reforming is a well-established process, it suffers from the following disadvantages.

1. It is highly endothermic process and hence, energy requirements are very high.
2. H_2/CO ratio obtained in the product stream is very high (>3) and therefore is unsuitable for methanol and Fischer-Tropsch syntheses.
3. The CO selectivity obtained is very poor because of the water gas reaction.

4. The catalyst undergoes deactivation very fast due to coke deposition on the surface of the catalyst, which results in the poor heat transfer from wall of the reactor.

1.1.2.CO₂ Reforming of Methane to Syngas

Release of large quantities of CO₂ in the atmosphere has created a large greenhouse effect causing a global warming. Hence worldwide efforts are being made for the conversion of CO₂ to useful products. One of the ways of activating CO₂ is its reaction with methane to carbon monoxide, commonly known as CO₂ reforming of methane.

Reforming of methane with CO₂ to produce synthesis gas with a H₂/CO ratio of approximately 1 has to date no significant applications by itself. The Calcor process employs CO₂ reforming of hydrocarbons to produce syngas. It is not clear whether this process has yet been commercially exploited. Nevertheless the reforming of methane with CO₂ has been used in conjunction with widely applied steam/methane reforming process when H₂/CO ratio of the product gas is required to be less than that generated by steam reforming alone.

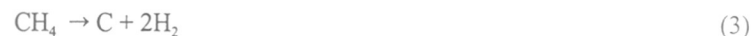
The most intriguing and challenging problem underlying the CO₂ reforming of methane to syngas is coking. During the past decades the process of carbon dioxide reforming of methane has received considerable attention and efforts have been focussed on the development of the catalysts which show high activity towards synthesis gas formation and also resistant to coking, thus displaying long term carbon-free operation. A review (147) on the chemistry of methane reforming with CO₂ and its current and potential applications ha also appeared.

Thermodynamics of CO₂ Reforming of Methane

The CO₂ reforming of methane involves a highly endothermic reaction (Equation-1). The thermodynamics and equilibrium characteristics of CO₂ reforming of methane are similar to the widely employed steam reforming of methane (Equation-2) except that the former reaction produces synthesis gas with lower H₂/CO ratio, viz.,



The CO₂ reforming of methane has been used in conjunction with steam reforming process and the coupled reactions are likely to be conducted under conditions where carbon formations via reactions ,



is thermodynamically feasible. Other reactions which could also have an important influence on the overall product spectrum are:



Thus, the CH_4/CO_2 reforming reaction (Eq. (1)) can be seen as consisting of reactions (3) and the reverse reaction (4). The carbon formed in reaction (3) should be rapidly consumed by the reverse of reaction (4) and, to a lesser extent, by the steam carbon gasification reaction (i.e., reaction (6)). Reaction (6) can play a role in CO_2/CH_4 reforming because steam is almost always formed via the reverse water gas shift (RWGS) reaction (Eq. (5)). If the reaction (3) is faster than the carbon removal rate(s), there will be a net build-up of carbon to pose serious problems and reactor blockages. Apart from reaction (3), reaction (4) and the reverse of reaction (6), both which are favoured at low temperatures, are also potential sources of carbon. It may also be noted that reaction (5), which consumes product hydrogen, represents a disadvantage unless both reactions (5) and (6) are made to take place efficiently in tandem so that the overall stoichiometry of the CO_2/CH_4 reforming reaction is maintained.

Apparently, the role of suitable catalysts would be not only to speed up the overall reaction but also to adjust the appropriate elementary steps in a way which prevents both net carbon deposition and water formation. It, therefore is relevant to carry out literature survey on the catalysis of the CO_2 reforming of methane to know if carbon deposition (a problem of serious magnitude) and water formation can be prevented in suitable catalyst systems.

A 5-15 mol% Ni supported on $\gamma\text{-Al}_2\text{O}_3$, SiO_2 or MgO (20, 26, 30), 32 mol% Ni/ $\alpha\text{-Al}_2\text{O}_3$ (25), 3.0 mol% Ni/MgO or Mg-Ca-Oxide (33, 34), 1.0 mol% Ru/MgO (26), 7.0 mol% Ru/MgO (23), 0.4-1.0 mol% Ru/ Al_2O_3 , silicified Al_2O_3 or silicified MgO (22-24, 25), 1.0 mol% Rh/MgO & Pd/MgO (28), 1.0 mol% Pd/ $\gamma\text{-Al}_2\text{O}_3$ (20, 22), 0.5-1.9 mol% Ir/ $\gamma\text{-Al}_2\text{O}_3$ or Eu_2O_3 (20, 22, 23) 23.0 wt% Co quartz-Na silicate (29), Cu (30), and 17.0 mol% Cu/ SiO_2 (31) represent those elements which are reported to be active for CO_2/CH_4 reforming in fixed bed reactor at 1 atmosphere. The relatively small number of data of the important catalysts is largely a reflection of the fact that the number of catalysts evaluated so far is limited, but the list of active catalysts is likely to grow as a result of future research efforts. The earlier studies for CO_2 reforming of methane to CO and H_2 over different catalysts at atmospheric under given reaction conditions are summarized in Table 1.1.2

Table 1.1.2. Summary of Earlier Work on the CO₂ Reforming of Methane to Syngas over Noble Metal Catalysts.

Catalyst	Reaction conditions			Remarks, if any	Authors (year)	Ref
	Temp. (°C)	Feed (CH ₄ :CO ₂ :dil.)	W/F, GHSV or contact time			
5.0 wt% Pd/support Support=TiO ₂ ,Al ₂ O ₃ ,Na- aY,SiO ₂ ,MgO,Na- ZSM-5	500	1.0:1.0:2.0	0.6 s	Catalysts prepared using titania and alumina as a support material show much better performance than zeolites, silica or MgO.	Masai et al ((1988))	32
Rh/Al ₂ O ₃ or 0.5 wt% Ru/Al ₂ O ₃	600-800	1.0 : 1.0 : 0.0	51-10 ³ x10 ³ h ⁻¹	A model has been constructed for conv. in pellet by incorporating both the reverse reaction and the effect of external and internal diffusion. When tested with experimental data, it gave good agreement with conversion and product distribution.	Richardson & Parpatiyadar (1990)	21r
1.0 wt% Ir or Ru/Al ₂ O ₃	777	1.0 : 1.0 : 0.0	2 x 10 ⁴ h ⁻¹	An alternative catalytic strategy for CO ₂ reforming which give excellent yield from a stoichiometric (1:1) of feed has been described The carbon deposition has been found to be suppressed to a significant extent.	Ashcroft et al (1991)	20
1.0 wt% Pt/Al ₂ O ₃	50	CO ₂ : CH ₄ : dil. 0.0-1.6 : 1.0 : 0.0	4.14 g s ml ⁻¹	The product composition (other than water) has been observed in a catalytic experiment as a function of CO ₂ / CH ₄ feed ratios.	Gaustafson et al (1991)	36

Table 1.1.2 continued

1.0 wt% Pt, Pd, Rh, Ru, or Ir on Al ₂ O ₃	450-550	1.0 : 1.0 : 0.0	3.0 x 10 ³ h ⁻¹	The specific activity of the catalysts decreased in the order : Ru, Pd, Rh, Pt and Ir which agreed with their activity order towards dissociation of CO ₂	Solymosi et al (1991)	27
1.0-5.0 wt% Ru or Ir/Eu ₂ O ₃	400-700	1.0	1.12x 10 ⁴ h ⁻¹	Both the catalysts have been reported to be efficient ones which showed no coke formation even after prolonged usage.	Perera et al (1991)	23
Ni, Ru, Rh, Pd, or Ir catalysts.	500-650	1.0	—	The authors compared various metals for CO ₂ reforming using the methods for studying the equilibrium of coke forming reaction, and the catalytic activity for carbon formation in the process.	Rostrup & Hansen (1993)	28
1.0 wt% Rh/support (support=TiO ₂ , Al ₂ O ₃ , MgO, SiO ₂)	500	1.0	6.0 x 10 ³ h ⁻¹	The detailed kinetic measurements with due emphasis on interaction of CH ₄ with Rh on the effect of different supports, have been reported..	Erohelyi et al (1993)	39
Rh/Al ₂ O ₃ , or SiO ₂	277-727	3.4 : 3.4 : 93.2	3.0 x 10 ⁴ cm ³ . g ⁻¹ . h ⁻¹	The possible model of synergetic effect has been proposed	Nakamura et al (1994)	42

Table 1.1.2 continued

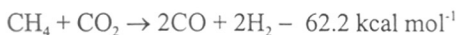
Thin Pd film (20 μ m) supported on outer surface of porous alumina cylinder	500	—	—	The methane conversion exceeded the equilibrium attainable in the conventional system, since use of H ₂ permeable membrane shifted the thermodynamic equilibrium towards right hand side.	Kikuchi et al (1997)	50
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1.1.3 Simultaneous CO₂ and Steam Reforming of Methane to Syngas

Release of large quantities of CO₂ in the atmosphere has created a large greenhouse effect causing a global warming. Hence worldwide efforts are being made for conversion of CO₂ to useful products. One of the ways of activating CO₂ is its reaction with methane to carbon monoxide and hydrogen, commonly known as CO₂ reforming of methane. In the last few years, the research activities on the CO₂ reforming of methane have gained a lot of momentum.

In the simultaneous CO₂ and steam reforming reaction, following reactions occur during the process.

Main reaction



Side reaction

No side reaction occurs during the above process.

In the last several years, few studies on the simultaneous CO₂ and steam reforming of methane to syngas have been carried out. The brief account of the work reported in the literature is given below.

Solymsi and coworkers (152) studied the CO₂ reforming, steam reforming and simultaneous steam and CO₂ reforming of methane at 427-500° and at 850°C on supported Ir catalysts in a fixed-bed continuous-flow reactor. In addition, the dissociation of CO₂, the low temperature interaction of CO₂ with methane, and the effects of supports have been also examined. The dissociation of CO₂, detected by IR spectroscopy, is greatly promoted by the presence of methane. The reaction between CO₂ and methane occurred rapidly above 400°C to give CO and H₂ with ratio of 1.0-3.7. The highest specific activity was measured for Ir/TiO₂. In the presence of water, H₂ was dominant reaction product due to the water gas shift reaction. Using a stoichiometric gas mixtures, carbon deposition was very limited in all the three reactions. Kinetic parameters of the reaction were detected and a possible reaction mechanism has been proposed.

Qin and Lapszewicz (153) investigated the activity of mixed steam and CO₂ reforming of CH₄ to produce synthesis gas was investigated and compared with and compared with those of steam reforming alone CO₂ reforming alone at 600-900°C under atm. pressure on MgO-supported noble metals. Mixed reforming showed a far lower methane conversion than the

value for thermodynamic equilibrium. The activity decrease following the order Ru, Rh > Ir > Pt > Pd. Little deactivation was observed for Ru, Rh and Ir catalysts. An isotopically labeled $^{13}\text{CO}_2$ experiment was carried out in-situ for mixed reforming on Rh/MgO; the results suggest that the CO_2 dissociates as CO-M and O-M (M = metal surface). The results of the temperature programmed reaction of mixed reforming showed that the reforming and steam reforming start simultaneously. A possible reaction mechanism was discussed.

Choudhary and Rajput (149) have investigated the steam reforming, CO_2 reforming, and simultaneous steam and CO_2 reforming of methane to CO and H_2 over NiO-CaO catalyst (without any prereduction treatment) at different temperatures (700-850°C) and space velocities (5000-70,000 $\text{cm}^3 \text{g}^{-1} \text{h}^{-1}$). The catalyst is characterized by XRD, XPS, and temperature programmed reduction (TPR). The catalyst showed high activity/selectivity in both the steam and CO_2 reforming reactions and the simultaneous steam and CO_2 reforming. In the CO_2 reforming, the coke deposition on the catalyst is found to be very fast. However, when the CO_2 reforming is carried out simultaneously with the steam reforming, the coke deposition on the catalyst is drastically reduced. By the simultaneous CO_2 and steam reforming (at $\geq 800^\circ\text{C}$ and space velocity of about 20,000-30,000 $\text{cm}^3 \text{g}^{-1} \text{h}^{-1}$), methane can be converted almost completely to syngas with 100% selectivity for both CO and H_2 . The H_2/CO ratio in the products can be varied between 1.5 and 2.5 quite conveniently by manipulating the relative concentration of steam and CO_2 in the feed.

Choudhary and coworkers (150) have investigated the conversion of methane to CO and H_2 by CO_2 reforming, steam reforming and by both the reactions occurring simultaneously over $\text{Co}_x\text{NiO}_{1-x}$ ($x = 0.0-0.5$) supported on commercial macroporous silica-alumina catalyst carrier (SA-5205, obtained from M/S Norton Co. U.S.A.) precoated with MgO at different temperatures (700°-900°C) and contact times (0.025-0.29 s at STP). With the increasing Co/Ni ratio of the catalyst, its surface area is decreased and its degree of reduction in TPR (by H_2) from 100° to 900°C is increased. The influence of Co/Ni ratio of the catalyst and feed ratios ($\text{H}_2\text{O}/\text{CH}_4 = 0.4 - 4.0$ and $\text{CO}_2/\text{CH}_4 = 0.3 - 1.2$) on the conversion and selectivity or H_2/CO product ratio has also been thoroughly investigated. With the increase of the Co/Ni ratio, the methane conversion and CO selectivity in the steam reforming is decreased, the carbon deposition on the catalyst during the CO_2 reforming is reduced drastically and the conversion of methane and CO_2 , H_2 selectivity and H_2/CO ratio in the CO_2 reforming is passed through a maximum and also the

Table 1.1.2. Summary of Earlier Work on the CO₂ Reforming of Methane to Syngas Over Non-Noble Metal Catalysts

Catalyst	Reaction conditions			Remarks, if any	Author(s) (Year)	Ref
	Temp. (°C)	Feed (CH ₄ :CO ₂ :dil.)	W/F, GHSV or contact time			
Ni/SiO ₂	700-900	2.0:1.0:0.0	3300 h ^{-h}	Calculations of the carbon deposition threshold for the CO ₂ -CH ₄ system have been done.	Frenkel et al (1986)	35
Sulphur passivated catalyst	900	—	—	The thermodynamic calculations for H ₂ O-CO ₂ -CH ₄ systems have been performed and it shown that using CO ₂ /CH ₄ feed ratio of 1/1 leads to the carbon deposition. The carbon formation can be prevented if sufficient amount. of steam is introduced.	Dibbern et al (1986)	19
Ni/Ni-MgO-Al ₂ O ₃ (1.0:4.0:5.0)	927	2.5-3.8:1.0	18-22 h ⁻¹ (WHSV)	Compositions to yield solid solutions were prepared by copptn. and firing. Such catalysts suppressed the carbon deposition	Gadalla et al (1989)	24
Ni/MgO/CaO	700-900	1.0	1.2 g.h.mol ⁻¹	Higher CaO containing. catalysts showed excellent stability under conditions such as 850°C and CO ₂ /CH ₄ = 1.1	Yamazaki et al (1992)	33
Ln ₂ Ru ₂ O ₇ (Ln=Nd, Sm, Eu, Gd) and Ln ₂ Ir ₂ O ₇ (Ln=Eu) pyrochlores	—	—	—	The catalysts have been studied in situ by EDXRD, which showed that the oxides are reduced to the Pt group metals, the iridate by a second order kinetic and ruthenates by first order kinetic reaction.	Ashcroft et al (1993)	40

Table 1.1. 2 continued.

Ni/Al ₂ O ₃ catalyst	600-750	2.0 : 1.0 : 0.0	3.0-7.7 x 10 ³ h ⁻¹	The filamentous carbon with a hollow inner channels was observed with Ni particles on the tip of carbon.	Yang & Chen (1994)	41
NiO/alkaline earth metal oxides (viz., MgO, SrO, BaO or CaO)	790	1.0 : 1.0 : 0.0	6.0 x 10 ⁴ h ⁻¹	NiO/MgO catalyst showed excellent activity. The presence of MgO inhibits the Boudouard reaction as shown by TPD of CO over this catalyst, which is attributed to the formation of NiO/MgO solid solution.	Ruckenstein & Hu (1995)	43
17.0 wt% Ni/La ₂ O ₃ , CaO, γ-Al ₂ O ₃ or Ni/(10 wt%)/γ-Al ₂ O ₃	750	1.0 : 1.0 : 3.0	—	Comparative study of methane over NiO/La ₂ O ₃ and conventional Ni-based catalyst has been done.	Zhang et al (1996)	44
Ni/SiO ₂ , C or TiO ₂	450-523	1.0:1.0:8.0	1.0-2.0 x 10 ⁴ .h ⁻¹	The role of support regarding carbon deposition and catalytic activity for CO ₂ reforming has been investigated over Ni-catalysts	Bradford & Vannice (1996)	45
A series of Ni/Al ₂ O ₃ catalysts	650-850	1.0	1.1 x 10 ⁴ h ⁻¹	The influence of promoters and catalyst prepn. techniques for CO ₂ reforming of CH ₄ over these catalysts has been studied	Chang et al (1996)	46

Table 1.1. 2 continued.

1.0 wt% Ni/SiO ₂ or Al ₂ O ₃ , 13.6 wt% Ni/SiO ₂ or TiO ₂	790	1.0	$6.0 \times 10^4 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$	The role of support over series of nickel catalysts has been highlighted	Ruckenstein & Hu (1996)	47
Ni/Al ₂ O ₃ catalyst contg. Na, K, Mg and Ca	500-800	1.0:1.0:4.0	$4.4 \times 10^4 \text{ h}^{-1}$	The carbon deposition in the CO ₂ reforming of CH ₄ was suppressed due to addition of Na, K, Mg and Ca metals to the catalyst.	Horiuchi et al (1996)	49
NiO-CaO	850	CO ₂ /CH ₄ =1.0	$11,500 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$	The time-on-stream activity/selectivity and pressure drop across the catalyst bed in CO ₂ reforming of methane to syngas has been studied	Choudhary & Rajput (1996)	149
NiO-MgO supported on SiO ₂ , Al ₂ O ₃ , SiC, ZrO ₂ and HfO ₂	700-800	CH ₄ /O ₂ =1.8	4.8 ms (at STP)	In case of NiO on different supports precoated with MgO, MgO avoids chemical interactions of NiO with active components of support, and stabilizes nickel on support against sintering by forming NiO-MgO solid solution	Choudhary et al (1997)	148
Modified Ni/Al ₂ O ₃ Modifiers = Co, Cu, Zr, Mn, Mo, Ag, & Sm	650	1.0: 1.0: 4.0	$7.2 \times 10^4 \text{ l Kg}^{-1} \text{ h}^{-1}$	Mn promoted catalyst showed a remarkable reduction in coke deposition entailing a small reduction in catalytic activity as compared to the unmodified one.	Coi, et al (1998)	85

Table 1.1.2 continued

Ir supported on TiO ₂ , ZrO ₂ , Y ₂ O ₃ , Al ₂ O ₃ , La ₂ O ₃ , MgO & SiO ₂	600	CH ₄ /CO ₂ =1.0	3.6 x 10 ⁴ h ⁻¹	The support activity order in the CO ₂ reforming of methane was reported to be as follows: TiO ₂ ≥ ZrO ₂ ≥ Y ₂ O ₃ > La ₂ O ₃ > SiO ₂	Nakagawa et al (1998)	51
NiO-MgO with Cr ₂ O ₃ , La ₂ O ₃ , dopants	780	CH ₄ /CO ₂ =0.98	6.0 x 10 ⁻⁴ ml g ⁻¹ h ⁻¹	Studies of XRD, XPS & H ₂ TPR showed that doping of small amounts of Cr ⁺³ , La ⁺³ to the Ni-MgO system led to the formation of host-dopant type Ni-Mg-Cr-La-O solid solution	Chen et al (1998)	52
NiO/MgO/SA-5205	700-900	CH ₄ /CO ₂ =1.1	1.0-9.5 x 10 ⁴ cm ³ g ⁻¹ h ⁻¹	Influence of the reaction temperature and the space velocity on the conversion, H ₂ selectivity and H ₂ /CO ratio in the process has been studied.	Choudhary et al (1998)	138
NiO-MgO and NiO-CoO-MgO catalysts	850	CH ₄ /CO ₂ =1.1	13,500 cm ³ g ⁻¹ h ⁻¹	The influence of time-on-stream activity on the conversion and pressure drop across the reactor (which is the measure of filamental carbon deposition) has been studied	Choudhary and Mamman (Present work)	140

conversion, particularly of methane, in the simultaneous steam and CO₂ reforming is passed through a maximum, at the Co/Ni ratio of about 0.17. The supported catalyst with Co/Ni ratio of 0.17 shows high methane conversion activity (methane conversion > 95%) and 100% selectivity for both CO and H₂ with H₂/CO ratio varying from 1.2 - 2.2 in the simultaneous steam and CO₂ reforming processes at high and space velocity (24,740 cm³ g⁻¹ h⁻¹). The H₂/CO ratio can be controlled by manipulating the H₂O/CO₂ ratio in the feed, it is increased with increasing the H₂O/CO₂ ratio and vice versa.

1.1.4 Autothermal Process for Syngas Production

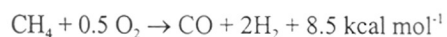
Autothermal reforming of methane is a combination of non-catalytic partial oxidation and steam reforming developed by Haldor-Topsoe in the late 1950's with the aim of performing reforming in a single reactor [17]. The reformer basically consists of a ceramic lined tube, similar to O₂ fired secondary reformer used in steam reforming of methane process, and a fixed catalyst bed reactor for equilibration of the gas.

The preheated feed streams (CH₄ + H₂O, and H₂O + O₂) are mixed in a burner placed at the top where partial oxidation of methane reactions take place. Typically, ATR operates at high temperature ca. 1930°C in the combustion zone and 930-1130°C in the catalyst zone. This results in a lower O₂ consumption (O₂/CH₄ = 0.55-0.60), however with a certain amount of steam added to feedstock to eliminate carbon formation. The carbon and soot formation in the combustion zone is an undesired reaction which leads to carbon deposition on downstream tubes causing equipment damage, pressure losses and subsequently heat transfer problems.

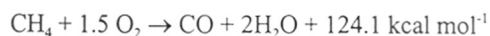
1.1.5 Partial Oxidation of Methane to Syngas

Catalytic partial oxidation of methane to syngas offers the most viable alternative to the steam reforming process. It is mildly exothermic reaction which produces H₂ and CO with the desirable H₂/CO ratio of 2.0, suitable for various down stream processes such as Fisher-Tropsch and methanol synthesis processes. The reactions which occur during the partial oxidation of methane to syngas are given below.

Main reaction



Side reactions



Extensive studies on the partial oxidation of methane to syngas have been done in the last several years. A few reviews (145, 146, 151) on this subject have also appeared. A brief account of the work done in the partial oxidation of methane to syngas is presented in the Table 1.1.3

1.1.6 Coupling of Exothermic and Endothermic Reactions in the Methane-to-Syngas Conversion

Catalytic oxidative conversion of methane to syngas (a mixture of CO and H₂), at a very low contact time (1-2 ms at the reaction conditions) (68, 69, 74, 76, 79, 81, 84, 87, 129-131), is a process of great practical importance. This process, unlike the conventional steam reforming process, is mildly exothermic and hence, not at all energy intensive and moreover, it can provide syngas with H₂/CO product ratio (about 2.0), suitable for the methanol and/or Fischer-Tropsch synthesis processes without any downstream processing. A number of nickel, cobalt and/or noble metal containing catalysts [viz., NiO-MgO (68), NiO-CaO (76), CoO-MgO (77), CoO or NiO-rare earth oxides (69, 81), LaNiO₃ (129), Ni/Al₂O₃ with or without Pt (79), supported noble metals (74, 76, 87), NiO-CoO-Yb₂O₃ or -ZrO₂ or -ThO₂ (151), NiO supported on commercial low surface area catalyst carriers precoated with alkaline and rare earth oxides (130, 131), showing high activity and selectivity at a very low contact time (1-2 ms), have been reported for this process.

In all the above studies, the amount of catalyst used was very small (≤ 20 mg) and hence, there was no serious problem for the removal of heat from the reactor. But, when large amount of catalyst (1.0 gm) was used, it was extremely difficult to control the reaction because of the limitations imposed by heat removal from the reactor. The oxidative methane-to-syngas conversion process is highly hazardous and difficult to practice, inspite of the fact that the partial oxidation of methane to CO and H₂ is mildly exothermic ($\Delta H_r = - 5.4$ kcal mol⁻¹) and the selectivity is high (95%). This is because of the fact that a very low contact time coupled with high conversion ($\geq 90\%$) results in production of a large amount of heat in a very small catalyst zone, the removal of which is very difficult. Moreover, a small decrease in the selectivity by some reason, can result in a drastic increase in the heat produced due to the combustion of methane to CO₂ and water, making the process control still more difficult and/or leading to process run-away. In order to overcome this limitation, efforts have been made to carry out the exothermic oxidative methane-to-syngas conversion simultaneously with the endothermic steam reforming of methane (138, 141), or CO₂ reforming of methane (20, 138, 142) or with both

Table 1.1.3 Summary of the Studies on the Oxidative Conversion of Methane to Syngas over Noble Metals

Catalyst	Reaction conditions			Remarks, if any	Author(s) Year	Ref
	Temp. (°C)	Feed composition	GHSV/Contact time or W/F			
1.0 wt% Ru, Rh, Pd or Pt/Al ₂ O ₃	777	2.0	4.0 x 10 ⁴ h ⁻¹	The yield of CO and H ₂ improved with increasing temp. from 377° to 777°C and decreased with increasing pressure between 1 & 20 atm.	Vernon et al (1990)	60
Pd/Sc ₂ O ₃ , La ₂ O ₃ , ZrO ₂ , HfO ₂ , CeO ₂ , TiO ₂ , Al ₂ O ₃ , SiO ₂	100-750	CH ₄ :O ₂ =4.0- 8.0	5.0 x 10 ³ h ⁻¹	The authors proposed that methane is adsorbed to form a surface CH ₃ species and desorbs to form CO ₂ in gas phase. The surface CH ₃ species results in the formation of CH _x intermediate species to form CO.	Bhattacharya et al (1992)	70
Pd/Al ₂ O ₃	498	1.5	—	The substoichiometric O ₂ atmosphere (O ₂ /CH ₄ < 2), CO formation was observed as soon as O ₂ had been consumed. It becomes the main product for the lowest oxy-to-methane ratio (0.66).	Mouddib et al (1992)	71
Pt and Pd deposited on ceria stabilized γ- Al ₂ O ₃	—	—	10-30 ms	The axial temperature profiles and the product analysis revealed that the combustion occur at the inlet of honeycomb, with reforming and shift reactions occurring downstream to yield CO & H ₂	Houchmuth (1992)	72

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Table 1.1.3 continued

Rh/SiO ₂	700	2.0	1.2 x 10 ⁴ h ⁻¹	The catalyst showed onset of catalytic activity at temp. > 600°C	Kumimori et al (1992)	73
RhVO ₄ /SiO ₂	700	2.0	1.2 x 10 ⁴ h ⁻¹	The catalyst showed the onset of catalytic activity at temperature around 500°C. The authors suggested that different catalytic activity may be due to change in morphology (Rh dispersion) and Rh-vanadia interaction	Kumimori et al (1992)	73
Pt & Pt-Rh coated monoliths	1100	19-23% CH ₄ in air	1 x 10 ⁻⁴ -10 ⁻²	—	Hickman et al (1992)	74
SiO ₂ supported Rh, Ru and Ni catalysts	627	2.0	0.15 s	The authors subscribed to the theory of total oxidation followed by reforming & shifts reactions to explain the observed results.	Nakamura et al (1993)	82
Pd/ZrO ₂	600	8.0	—	At high temperatures, the reaction was reported to be influenced by the formation of carbonaceous deposits on the surface of catalyst.	Marti et al (1993)	83
10 wt% Pt or Rh/Al ₂ O ₃	850-1250	1.8	1.0 x 10 ⁶ h ⁻¹	Rhodium catalyst has been reported to be superior to Pt. This has been explained by the known chemistry & kinetics of reactants, intermediates, & products on these surfaces.	Hickman et al (1993)	84

Table 1.1.3 continued

Pt & Rh/alumina foam monoliths	327-1227	—	—	—	An elementary-step model (19 steps) has been developed using rate parameters from the literature. The consistency of the model and the exptl. results strongly suggest that H ₂ & CO are primary products of POM to syngas via a pyrolysis mechanism under methane-rich conditions and at high temperatures.	Hickman & Schmidt (1993)	86
0.5 wt% Rh, Ru, Pt, Pd/MgO	500-950	CH ₄ /O ₂ =2.0	1.0 x 10 ⁻⁶ cm ³ g ⁻¹ h ⁻¹		The relationship between the characteristics of partial oxidation catalysts and their ability to activate methane molecule has been studied.	Lapszewicz & Jiang, (1993)	87
1.0 wt% Ru, Rh, Pd, Ir or Pt Supported on Al ₂ O ₃	777	CH ₄ : O ₂ : N ₂ (2.0 : 1.0 : 4.0)	4.0 x 10 ⁴ h ⁻¹		The relative rate of carbon deposition follows the order : Ni. >Pd, Rh > Ir, negligible carbon deposition occurred on Ir, even after 200h.	Claridge et al (1993)	89
0.2 & 0.5 wt% Rh/Al ₂ O ₃	550	2.0	1.5-6.5 x 10 ⁵ g ml ⁻¹		Particular attention has been paid to remove heat transport limitations and to identify the reaction conditions within the kinetic controlled regime.	Verykios et al (1994)	91

Table 1.1.3 continued

4.0 wt% Pt/Al ₂ O ₃	900-1100	1.8	1.0x10 ⁶ h ⁻¹	The metal films on the ceramic monoliths are preferred to metal gauzes which become too brittle in excess of hydrocarbons. The variation in selectivity and conversion on different metals is key in designing useful reactor systems.	Schmidt et al (1994)	93
3.5 wt% Pd/La ₂ O ₃	1200	2.0	1.0x10 ⁵ h ⁻¹	The catalyst is reported to undergo deactivation due to the formation of coke leading to the pore blockage.	Tornainen et al (1994)	94
0.5 wt% Pd/monolith	1270	2.	1.0x10 ⁵ h ⁻¹	Same as above	Tornainen et al (1994)	94
5 wt% Ni/monolith & 1.5 wt% Pt/monolith.	600-900	2.0	0.2-.005 s	The axial temperature profile in the catalyst indicates that the overall reaction consists of total oxidation followed by endothermic reforming and WGS reactions	Heimes et al (1994)	95
0.5 wt% Pt/Al ₂ O ₃	800	2.0	4.0x10 ³ h ⁻¹	The authors have suggested that fluidized beds offer viable energy-efficient alternative reactor configurations for syngas production by the catalytic oxidation of methane to syngas	Schmidt et al (1994)	96
Pt/10.0wt% gauze catalyst	200-1050	CH ₄ :O ₂ :Ar (2.0:1.0:10.0)	1.5 to 5.0x10 ⁻⁴ s	The products with compositions far from equilibrium were obtained	Hofstad et al (1997).	102

Table 1.1.3 continued

0.1 wt% Pt and Rh monoliths	600-800	CH ₄ :O ₂ :Ar (2.0:1.0:10)	1.0x10 ⁻³ -4.0x 10 ⁻²	—	Hofstad et al (1997)	104
Ru supported on SiO ₂ , γ-Al ₂ O ₃ , YSZ, or TiO ₂	550-750	—	—	Isotopic labeling expts. demonstrated that direct partial oxidn. route is responsible for the high CO & H ₂ selectivity at low CH ₄ conv. obsd. over the Ru/TiO ₂ catalysts	Boucourvalas et al (1997)	105
Rh/α-Al ₂ O ₃	1000	—	—	The POM to syngas has been studied close to industrially relevant conditions (viz., high temperature and 800 kPa)	Slaa et al (1997)	110
3.0 wt% Rh/TiO ₂	—	—	—	The membrane reactor allows the reaction to be performed without premixing & thus reducing the risk of explosion at low CH ₄ /O ₂ ratios.	Alibrando et al (1997)	114
Rhodium catalyst	—	—	1.0 x 10 ⁻² s	Small surface rhodium carbonyl clusters were generated at a short contact times	Basini et al (1997)	124
1.0 wt%Pt/CeO ₂ and CeO ₂	400-800	—	—	Authors suggested that the synthesis gas was directly formed from CH ₄	Otsuka et al (1997)	125
CeO ₂ or Pt black/CeO ₂	—	—	—	The addition of Pt black accelerated the formation rates of H ₂ and CO and decreased the activation energy for their production.	Otsuka et al ((1998)	115

Table 1.1.3 continued

5.0 wt% Ir/TiO ₂	600	5.0 s	—	The active species of Ir/TiO ₂ was found to be Ir ⁰ by XPS.	Nakagawa et al (1998)	116
Rh sponge diluted with SiC or Al ₂ O ₃ and 0.3 wt%Rh/Al ₂ O ₃	400-850	—	—	The reaction has been studied using the temporal-analysis-of products setup on different Rh catalysts.	Hofstad et al (1998).	117
Ru, Pd, Pt, Ni, Rh supported on γ -Al ₂ O ₃ , Pt, Rh/MgO, or ZrO ₂ and Rh powder	—	—	—	The study reveals that in POM to synthesis gas, CO ₂ is primary product	Baerns et al (1998)	122

Table 1.1.3 : Summary of the Earlier Studies of the Oxidative Conversion of Methane to Syngas over Non-Noble Metal Catalysts

Catalyst	Reaction conditions			Remarks, if any	Authors (Year)	Ref.
	Temp. (°C)	Feed composition	GHSV/Contact time			
10% refractory supported Nickel	725-900	2.0	6 - 42 s	The reforming reaction mechanism has been proposed for the oxidative conversion of methane to syngas.	Prettre et al (1946)	53
Ni/Mullite	760-900	25% CH ₄ in air	—	Diffusional effects on POM to syngas reaction have been studied	Huszar et al (1971)	54
Ni/α-Al ₂ O ₃ , Ni/ZrO ₂	570-760	1.3 - 1.7	—	Ni ⁰ formed during prereduction is responsible for POM reaction	Gavalas et al (1984)	57
Ni/Al ₂ O ₃	800-1000	Natural gas and O ₂	0.25 s	POM, with reversal of direction of flow (so as to obtain high temperature) has been studied adiabatically.	Blanks et al (1990)	58
Ln ₃ Ru ₂ O ₇ , Ln=Pr,Sm,Eu, Gd,Tb,Dy,Tm Yb,Lu	777	CH ₄ :O ₂ : N ₂ 2.0 : 1.0: 4.0	4.0 x 10 ⁴ h ⁻¹	The ruthenium analogues, Ln ₃ Ru ₂ O ₇ are extraordinarily active and selective catalyst for POM to syngas	Ashcroft et al (1990)	59

Table 1.1.3 continued

$\text{La}_2\text{MgP}_2\text{O}_6$	777	2.0 : 1.0 : 0.0	$4.0 \times 10^4 \text{ h}^{-1}$	It has been shown that POM to syngas can be carried out with yield in excess of 90% at a pressure of approximately 1 atm. & temperature close to 777°C.	Vernon et al (1990)	60
$\text{Eu}_2\text{Ir}_2\text{O}_7$	600	2.0 : 1.0 : 0.0	—	The POM has been studied in situ by using powder XRD and mass spectrometry. It was shown that the active catalyst comprised of iridium metal (30°A) supported on Eu_2O_3	Ashcroft et al (1991)	62
25.0 wt% $\text{Ni}/\text{Al}_2\text{O}_3$	700	1.8 : 1.0 : 25.0	0.09 s	The study revealed that the catalyst bed consisted of three regimes, viz., NiAl_2O_4 , $\text{NiO}+\text{Al}_2\text{O}_3$, and $\text{Ni}/\text{Al}_2\text{O}_3$ phase. The CO & H_2 formation occurs in the final $\text{Ni}/\text{Al}_2\text{O}_3$ phase.	Dissayanaya et al (1991)	63
DyRu_2O_7	777	2.0 : 1.0 : 0.0	$4.0 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$	The influence of pressure (1-20 atm.) over the catalyst has been studied. It is an important data for its use in industrial scale-up for F-T and methanol synthesis processes	Vernon et al (1992)	64
Undisclosed catalysts	—	—	—	The authors identified the reaction pathway and provided information for the development of suitable catalysts for industrial usage.	Lapszewicz et al (1992)	65
$\text{Pr}_2\text{Ru}_2\text{O}_7$	777	—	$4.0 \times 10^4 \text{ h}^{-1}$	The $\text{Pr}_2\text{Ru}_2\text{O}_7$ is reduced to Ru metal. Praseodymium oxide is reported to be active for methane conversion and Ru is active site for syngas formation.	Porier et al (1992)	66

Table 1.1.3 continued

Nickel based catalysts	—	—	—	—	The effect of temperature gradients in the catalyst bed was nicely illustrated. The author suggested that the POM to syngas consists of combination of exothermic combustion, WGS and of steam reforming reactions.	Vermeiren et al (1992)	67
NiO-MgO(Ni/Mg=1.0 & 3.0)	700	2.0	$5.0 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$	$5.0 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$	The authors reported preliminary, highly promising results on the POM to syngas at atmospheric pressure over NiO-MgO catalysts using an extremely high space velocities	Choudhary et al (1992)	68
Ni/Yb ₂ O ₃ (Ni/Yb=0.1-4.0)	700	2.0	$5.0 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$	$5.0 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$	Ni/Yb ₂ O ₃ showed a high activity/selectivity at wide range of temperatures. The process follows a reaction path totally different from that of high-temperature noncatalytic and catalytic processes.	Choudhary et al ((1992)	69
Ni-CaO(Ni/Ca=3.0) Reduced & unreduced catalysts	300-800	2.0	$5.0 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$	$5.0 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$	The product selectivity in the process is controlled by kinetics rather than its thermodynamics	Choudhary et al (1992)	76
Co-MgO (Co/Mg=0.1-10)	700	2.0	$5.0 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$	$5.0 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$	It has been shown that POM at 700°C and high space velocities used in the process do not involve the formation of CO ₂ and water, as initial products, followed by endothermic reactions of unconverted methane to CO & H ₂	Choudhary et al (1992)	77

Table 1.1.3 continued

CoO-RE Oxides	300-700	2.0	$5.0 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$	CoO-rare earth oxide catalysts (particularly CoO-Yb ₂ O ₃) showed high activity/selectivity in the oxidation of methane to syngas	Choudhary et al (1992)	78
Ni-Yb ₂ O ₃	300-700	2.0	$5.0 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$	The hot spots have been detected visually and with an optical pyrometer during the oxidation reactions.	Dissanayake et al (1993)	80
NiO-LnO _x Ln=La,Ce,Pr,Nd,S m,Eu,Gd,Tb,Dy,Er Yb	535-560	2.0	$5.0 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$	The pulse reaction of CH ₄ on NiO-Nd ₂ O ₃ (at 600°C) showed involvement of lattice O ₂ in the initial reaction and reveals the formation of C from CO on the catalyst reduced in the reaction.	Choudhary et al (1993)	81
SiO ₂ supported Rh, Ru and Ni catalysts	627	2.0	0.15 s	The authors subscribed to the theory of total oxidation followed by reforming & shifts reactions to explain the observed results.	Nakamura et al (1993)	82
5.0 wt% Re/Al ₂ O ₃	777	2.0	$2.0-5.3 \times 10^4 \text{ h}^{-1}$	The kinetic exptl. data showed that the activity of Re/Al ₂ O ₃ is low (35%) at lower temperature. The effect of temp. on its catalytic activity is due to the oxidation of Re to its oxide form.	Claridge et al (1994)	90
NiO-CaO	500	1.5-2.5	$5.0-50 \times 10^4 \text{ h}^{-1}$	The authors suggested that yield of syngas was found to deviate from the equilibrium values due to the temperature higher than actually measured one	Theron et al (1994)	92

Table 1.1.3 continued

5 wt% Ni/monolith & 1.5 wt% Pt/monolith.	600-900	2.0	0.2-005 s	The axial temperature profile in the catalyst indicates that the overall reaction consists of total oxidation followed by endothermic reforming and WGS reactions	Heitnes et al (1994)	95
Strontium hydroxyapatite	600-900		0.9 dm ³ h ⁻¹	The pretreatment of catalyst at 900°C generate new active sites on its surface in the form of structural defects.	Matsumura et al (1994)	97
Rh coated foam monolith	1000	2.0 : 1.0 : 0.0	2.7 x 10 ⁻³ s	The effect of pressure between 1 and 5 on the conversion and selectivities have been examined.	Dietz et al (1995)	61
18.7 wt% Ni/Al ₂ O ₃ (reduced & reduced catalysts)	50-800	1.8	5.0 x 10 ⁵ h ⁻¹	It has been concluded that using an extremely high space velocities results in a much higher selectivity & productivity with a change in a reaction pathway.	Choudhary et al (1995)	98
Two zone fixed bed of a Ni/Al ₂ O ₃ in ceramic membrane	800	CH ₄ : O ₂ : N ₂ (2.0 : 1.0 : 1.0)	—	The performance of the membrane reactor has been compared with that of fixed bed reactor.	Santos et al (1995)	99
Supported Nickel precoated with MgO, CaO or rare earth oxides	800	1.8	1.8 ms	Among the precoating metal oxides, the best performance is observed for MgO	Choudhary et al (1995)	130

Table 1.1.3 continued

20 Ni/La ₂ O ₃	400-750	Pulse of 45 μ l of CH ₄ and O ₂ ,	$3.0 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$	The transient response curves revealed that CO ₂ generation is delayed in comparison to that of CO, hence that CO is primary product and CO ₂ is subsequently generated on the catalyst during CH ₄ /O ₂ pulses.	Hu Ruckenstein (1996)	100
10.0 wt% Ni/SiO ₂	600-800	2.0	—	Use of CD ₄ instead of CH ₄ showed that the methane dissociation is a key step and that CO and CO ₂ are formed via a common intermediate.	Au et al (1996)	108
Ni/Ca aluminate	750	2.0	6.0 kg s mol ⁻¹	The difference in catalytic activity/selectivity for the POM reaction has been attributed to various degree of reducibility of the surface Ni species.	Goula et al (1996)	109
LaNiO ₃	800	1.8	$5.2 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$	LaNiO ₃ perovskite has been reported to be transformed to Ni ⁰ /La ₂ O ₃ during its operation in the catalyst process.	Choudhary et al (1996)	129
Alkali metal & rare earth metal oxides contg. NiO/Al ₂ O ₃ catalysts.	600-900	1.6-15.7	$2.7 \times 10^4 \text{ l kg}^{-1} \text{ h}^{-1}$	The catalysts were characterized by techniques such as flow reaction BET, XRD, CO chemisorption & TG analysis.	Miao et al (1997)	103

Table 1.1.3 continued

BaTi _{1-x} Ni _x O ₃ (x=0.0-0.4)	750-800	1.9	5.0 x 10 ³ cm ³ g ⁻¹ h ⁻¹	—	Shiozaki et al (1997)	106
Ni-HY Zeolites	—	—	—	TPR, CO chemisorption and XPS studies showed that the small clusters of Ni formed within the pores are the active centres.	Pena et al (19997)	107
LnCoO ₃ (Ln=La, Pr, Nd, Sm, and Gd)	736	2.0	2.0 x 10 ⁵ h ⁻¹	An evidence that the hydroxyl groups on the rare earth oxides in LaCoO ₃ system make some contribution to the reoxidn. of cobalt in the reaction via reverse spillover process has presented.	Lago et al (19997)	111
Ni-honeycomb catalyst ^b	700	2.0	—	Both methane conversion and CO & H ₂ selectivity approach that predicted by thermodynamic equilibrium	Gomez et al (1997)	112
Co and Ni based catalysts	600-900	—	—	A two-step process was proposed which lead to a detailed description of the catalytic bed under reaction conditions	Swaan et al (1997)	113

Table 1.1.3 continued

As above	600	Pulse of 0.9 ml of CH ₄ and O ₂	$3.0 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$	The activation energies of CH ₄ dehydrogenation in the presence and absence of O ₂ have been calculated using the bond order conservation Morse-potential approach.	Hu Ruckenstein (1995)	& 101
La ₂ O ₃ promoted NiO/Al ₂ O ₃ catalyst	—	—	—	The TPR & XRD measurements show that the addition of 2.0 wt% lanthana to the catalyst not only is the optimal content but also suppresses the carbon deposition in the reaction.	Cao et al (1997)	126
Ni/BaTiO ₃	800	—	—	The solid phase crystallization method bestows the catalyst with high nickel dispersion, strong metal support interactions between Ni and perovskite.	Shiozaki et al (1997)	127
NiO/SiO ₂ (reduced & fresh)	—	—	—	Reaction between CH ₄ and O ₂ occurred via Eley-Riedel mechanism over the unreduced NiO/SiO ₂ , and via Langmuir - Hinshelwood mechanism over the reduced NiO/SiO ₂ catalyst.	Hu et al (1998)	118
Ni/ α -Al ₂ O ₃ in fixed and fluidized bed reactors ^a	750-800	—	—	The CPOM reaction was influenced by the intraparticle mass transfer limitations.	Ostrwski et al (1998)	119

Table 1.1.3 continued

Ni/ α -Al ₂ O ₃	700-750	2.0	14.0 g s ml ⁻¹	Comparative study of POM to syngas in the fixed bed & fluidized bed membrane reactors have been carried out.	Ostrwski et al (1998)	120
NiO-MgO contg. trivalent-metal oxides viz., Cr ₂ O ₃ , La ₂ O ₃	780	—	—	Studies of XRD, XPS, and H ₂ -TPR showed that the addn. of dopants led to the formation of Ni-Mg-Cr-La solid soln. with considerable number of Schottky defects.	Chen et al (1998)	121
Ru, Pd, Pt, Ni, Rh supported on γ -Al ₂ O ₃ , Pt, Rh/MgO, or ZrO ₂ and Rh powder	—	—	—	The study reveals that in POM to synthesis gas, CO ₂ is primary product	Baerns et al (1998)	122
Co/carbon modified Al ₂ O ₃	—	—	—	All active and selective catalysts contain metallic cobalt in cubic form	Sokolovskii et al (1998)	123
Nickel supported catalyst	—	—	—	The oscillations of the temp. were observed.	Hu & Ruckenstein (1998)	128

Table 1.1.3 continued

Ni supported on catalyst carrier precoated with alkaline & RE oxides	850	1.8	5.1 x 10 ⁵ cm ³ g ⁻¹ h ⁻¹	The oxidative conversion of methane to syngas has been studied to elucidate the influence of precoating in the overall reaction.	Choudhary et al (1997)	131
NiO-MgO solid solution supported on low surface area catalyst carrier	600-900	1.8-8.0	6000-5,10,000 cm ³ g ⁻¹ h ⁻¹	Influence of time-on-stream, CH ₄ /O ₂ ratio in feed, space velocity, catalyst particle size, and its dilution by inert solid particles on the performance at different temps. has been investigated.	Choudhary et al (Present work)	132
Pt or Pd containing alkaline earth & rare earth oxides	700 & 800	1.8	5.1 x 10 ⁵ cm ³ g ⁻¹ h ⁻¹	The activity/selectivity of Pt-containing alkaline earth and rare earth oxide catalysts is better than the Pd-containing catalysts.	Choudhary et al (Present work)	134
Ni and/or cobalt containing ZrO ₂ , ThO ₂ , UO ₂ , TiO ₂ , and SiO ₂ catalysts	700	1.8	5.2 x 10 ⁵ cm ³ g ⁻¹ h ⁻¹	The influence of different metal oxide supports in the oxidative-to-methane syngas conversion at very low contact time has been investigated.	Choudhary et al (1998)	133
Pt- or Ru-containing NiO-MgO solid solution	500-800	1.8	5.1 x 10 ⁵ cm ³ g ⁻¹ h ⁻¹	The addition of Pt- or Ru- to NiO-MgO resulted in an increase in both the conversion & selectivity for both CO & H ₂ . The observed beneficial effects due to the spill-over of H atoms from noble metals to the NiO in the catalyst.	Choudhary & Mamman (Present work)	135

Table 1.1.3 continued

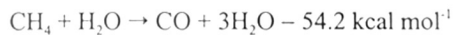
NiO-MgO, NiO-CaO, NiO-SrO, and NiO-mixed alkaline earth catalysts	700	1.8	$5.1 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$	The presence of higher alkaline earth oxide viz. SrO/or BaO causes large decrease or almost complete deactivation of the NiO-containing alkaline earth oxide(s) catalyst for the reaction	Choudhary et al (Present work)	136
NiALPO-5	500-900	1.8	as above	The catalyst showed good catalytic activity and selectivity at higher temperature.	Choudhary et al (Present work)	137

(129, 137, 138, 143); the exothermic and endothermic reactions could be coupled successfully, making the process energy efficient and non-hazardous or safer.

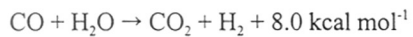
1.1.6.1 Oxy-steam reforming of methane to syngas

The following important reactions occur during the oxy-steam reforming of methane-to-syngas conversion reaction.

Main reaction



Side reaction

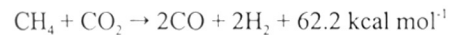
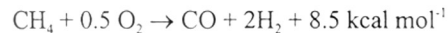


The work on the oxy-steam reforming of methane to syngas over different catalysts is summarized in Table 1. 1. 4.

1.1.6.2 Oxy-CO₂ Reforming of Methane to Syngas

Following important reactions take place during the oxy-CO₂ reforming of methane to syngas conversion process.

Main reactions



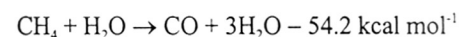
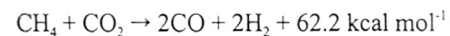
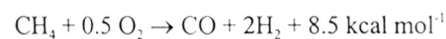
Side reaction



The summary of the work done on the oxy-CO₂ reforming of methane to syngas at 1 atmospheric pressure is presented in Table 1.1.5.

1.1.6.3 Simultaneous oxy-CO₂-and steam reforming of methane to syngas

In this process, the following reactions occur simultaneously



The studies on the simultaneous oxy-CO₂and steam reforming of methane to syngas are summarized in the Table 1 .1. 6.

Table 1.1.4 Results of Earlier and Present Studies of Oxy-Steam Reforming of Methane to Syngas at 1 atmosphere

Catalyst	Reaction conditions			Remarks, if any	Authors (year)	Ref.
	Temp. (°C)	Feed Composition	GHSV/Contact time			
NiO/MgO/SA-5205	800 & 850	CH ₄ /O ₂ =2.4 CH ₄ /H ₂ O=1.9-10.4	4.7 x 10 ⁻⁴ cm ³ g ⁻¹ h ⁻¹	The results reveal that the oxidative conversion of methane to syngas reaction occurs simultaneously with steam reforming and WGS reactions	Choudhary et al (1998)	138
Co _x Ni _{1-x} /MgO/SA-5205 (Co/Ni ratio = 0.17)	800 & 850	CH ₄ /(O ₂ +0.5H ₂ O) = 1.8	4.7 x 10 ⁻⁴ cm ³ g ⁻¹ h ⁻¹	The effect of reaction temperature, space velocity and CH ₄ /O ₂ feed ratio on the conversion, selectivity and H ₂ /CO ratio and the net heat of reaction in the process has been studied.	Choudhary et al (Present work)	139
NiO/MgO solid solution	700 & 800	CH ₄ /O ₂ =1.8-3.8 and CH ₄ /H ₂ O=1.44	4.9 x 10 ⁻⁴ cm ³ g ⁻¹ h ⁻¹	The effect of CH ₄ /O ₂ ratio in the feed on the conversion, selectivity and H ₂ /CO ratio and the net heat of reaction in the process has been studied.	Choudhary et al (Present work)	145
NiO-CoO-MgO	700 & 800	CH ₄ /O ₂ =1.8-3.8 and CH ₄ /H ₂ O=1.5	9500 cm ³ g ⁻¹ h ⁻¹	The study revealed that conversion of methane, CO selectivity and H ₂ /CO ratio are decreased but that of water & the value of ΔHr are increased markedly	Choudhary & Mamman (Present work)	140

Table 1.1.4 continued

NiO-CaO (Ni/Ca=3.0)	700-850	CH ₄ /O ₂ =1.8-6.0 CH ₄ /H ₂ O=1.6-10.0	16 x 10 ³ -1090 x 10 ³ h ⁻¹	By coupling of the exothermic oxidative conversion and the endothermic steam reforming of methane over the same catalyst, almost all the limitations of these two individual processes are eliminated.	Choudhary et al (1994)	141
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Table 1.1.5 Brief Summary of the Work done on the Oxy-CO₂ Reforming of Methane to Syngas

Catalyst	Reaction conditions			Remarks, if any	Authors (Year)	Ref.
	Temp. (°C)	Feed composition	GHSV/Contact time			
1.0 wt% Ir/Al ₂ O ₃	777	CH ₄ : O ₂ : CO ₂ (4.0 : 1.0 : 9.0)	2.0 x 10 ⁴ h ⁻¹	The study revealed that the POM and endothermic CO ₂ reforming reaction can be carried out simultaneously thus introducing the possibility of tuning the thermodynamics of the process.	Ashcroft et al (1991)	20
NiO-CaO (Ni/Ca=3.0)	700-900	CH ₄ /O ₂ =2.1CH ₄ /CO ₂ =8.0	10.0-50.0 x 10 ³ cm ³ g ⁻¹ h ⁻¹	The coupling of endothermic and exothermic reactions of methane with CO ₂ and O ₂ , respectively, over NiO-CaO catalyst results in its high conversion, selectivity and high productivity without catalytic deactivation for a long period in an energy efficient and safe manner	Choudhary et al (1995)	142
Ni/ALPO-5	750-900	CH ₄ /O ₂ =2.1, CH ₄ /CO ₂ =CH ₄ /CO ₂ =10.0	4.7 X 10 ⁵ cm ³ g ⁻¹ h ⁻¹	The NiO/ALPO-5 catalyst under operating conditions is in the form of NiO/AlPO ₄ (tridymite). The former is transformed into the later during the short initial reaction period at high temperature.	Choudhary et al (1997)	138

Table 1 1.5 continued.

NiO/MgO /SA-5205	750-850	CH ₄ /O ₂ =2.0-3.0, CH ₄ /CO ₂ =2.6- 9.4	4.58 x 10 ⁻⁴ cm ³ g ⁻¹ h ⁻¹	The H ₂ selectivity is lower than 100% because of the reverse shift reaction occurring simultaneously with the oxidative conversion and CO ₂ reforming of methane to syngas.	Choudhary et al (1998)	139
NiO-CoO- MgO	800	CH ₄ /O ₂ = 2.5, CH ₄ /CO ₂ = 3.4	4.5 x 10 ⁻⁴ cm ³ g ⁻¹ h ⁻¹	The Oxy-CO ₂ reforming reaction over this catalyst, the exothermic and endothermic reactions are coupled making this reaction highly energy efficient and non hazardous or safe to operate.	Choudhary & Mamman (Present work)	140
Co _x Ni _{1-x} /MgO/SA- 5205 (Co/Ni ratio= 0-0.9)	800	CH ₄ /O ₂ =2.19- 2.5, CH ₄ /CO ₂ =2.3- 7.3	2.3-4.6 x 10 ⁻⁴ cm ³ g ⁻¹ h ⁻¹	The present study revealed that the CH ₄ and CO ₂ & H ₂ selectivity passed through maximum at Co/Ni ratio of 0.17, whereas, H ₂ /CO ratio is not affected significantly.	Choudhary et al (Present work)	140
NiO-MgO solid solution	700-850	CH ₄ /O ₂ =2.2, CH ₄ /CO ₂ =7.3	49200 cm ³ g ⁻¹ h ⁻¹	With the increase of temperature from 700 to 850°C, the conversion of methane & CO ₂ is increased, the selectivity for H ₂ is increased to a small extent, and the net heat of reaction is increased indicating the a decrease in process exothermicity.	Choudhary et al (Present work)	145

Table 1.1.6 Brief Summary of the Work done on the Simultaneous Oxy-CO₂ and-Steam Reforming of Methane to Syngas

Catalyst	Reaction conditions		Remarks, if any	Author(s) (Year)	Ref.	
	Temp. (°C)	Feed composition GHSV/Contact time				
NiO-CaO	700-900	CH ₄ /O ₂ =2.1, CH ₄ /CO ₂ =10.0 CH ₄ /C O ₂ =10.0	4.8 x 10 ⁴ cm ³ g ⁻¹ h ⁻¹	A simple packed bed reactor could be used which has much lower capital and process operation costs.	Choudhary et al (1994)	144
LaNiO ₃	800-850	CH ₄ /O ₂ = 2.0-3.65, CO ₂ /H ₂ O =1.0, CH ₄ /CO ₂ +0.5CO ₂ +0.5 H ₂ O) =1.8	4.7 x 10 ⁴ cm ³ g ⁻¹ h ⁻¹	By carrying out the simultaneous oxidative conv. and steam and CO ₂ reforming of methane, the process can be operated in a most energy efficient manner, requiring little or no external energy.	Choudhary et al (1996)	129
Ni/ALPO-5	850	CH ₄ /O ₂ =2.1-2.6, CH ₄ /CO ₂ =4.0-13.2	4.7 x 10 ⁴ cm ³ g ⁻¹ h ⁻¹	The methane-to-syngas conversion process involving simultaneous oxidative conversion & CO ₂ and steam reforming reactions occur over the catalyst in a most energy efficient and safe manner, requiring little or no external energy.	Choudhary et al (1997)	138
NiO/MgO/ SA5205	800 & 850	CH ₄ /O ₂ = 2.0-3.6 CH ₄ /(0.5 CO ₂ +0.5 H ₂ O) ratio =3.8-20.5	4.72 x 10 ⁴ cm ³ g ⁻¹ h ⁻¹	Due to the coupling of endothermic and exothermic reactions over the same catalyst, the process occurs in a most energy efficient and safe manner.	Choudhary et al (Present work)	139

Table 1.1.6 continued

$\text{Co}_x\text{NiO}_{1-x}$ /MgO/SA-5205 ($x = 0.0-0.5$)	800 & 850	$\text{CH}_4/\text{O}_2 = 2.15-3.5$ $\text{CO}_2/\text{H}_2\text{O}=1.0,$ $\text{CH}_4/(\text{O}_2+0.5\text{CO}_2+0.5$ $\text{H}_2\text{O})=1.8$	$4.6 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$	<p>The H_2/CO ratio is not influenced significantly by the addition of Co to the catalyst. Hence, the catalyst with high Co/Ni ratio is preferred for this process since it has higher stability against filamental carbon formation.</p>	Choudhary et al (Present work)	139
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1.1.6.4 Advantages of the coupling of exothermic and endothermic reactions in the methane-to-syngas conversion

By carrying out the endothermic and exothermic methane-to-syngas conversion reactions over the same catalyst, it is possible to

- Make the overall process mildly exothermic, near thermoneutral or mildly exothermic simply by manipulating the process conditions (viz. CH_4/O_2 and $\text{CH}_4/\text{H}_2\text{O}$ ratios and temperature).
- Operate the process in a most energy efficient manner as the heat produced in the exothermic reactions is used instantly by the endothermic reaction.
- Operate the process without any problem for the heat removal from the reactor.
- Operate the process in a most safe manner as the possibility of development of hot spots in the catalyst and/or process run-away conditions can be totally eliminated or drastically reduced due to a buffering action on the temperature resulting from the coupling of exothermic and endothermic reactions
- Operate the process with requirement of little or no external energy.
- Obtain high methane conversion (above 90 %) with 100 % selectivity for CO and/or H_2 and also high productivity at high space velocities ($\approx 80,000 \text{ h}^{-1}$ or even higher).
- Eliminate almost all of the drawbacks/limitations of the steam reforming and oxidative methane-to-syngas conversion processes.

Because of low adiabatic temperature rise or fall, it may be possible to develop methane-to-syngas conversion process operating in an adiabatic reactor with following major advantages:

- Very simple reactor with no arrangement to supply or remove heat.
- Requirement of little or no external energy.
- Low capital and process operation costs.

1.2 OBJECTIVES AND SCOPE OF THE PRESENT WORK

The work for the present Ph.D. thesis was undertaken as a part of the comprehensive research program in our laboratory for the development of highly active, selective and productive catalysts and the underlying processes for the catalytic conversion of methane into syngas in an energy efficient and safe manner, with the following objectives.

1) To study the performance of following catalysts for the oxidative conversion of methane to syngas

- NiO-MgO (Ni/MgO = 0.0 to 10)
- NiO-CoO-MgO (Ni+Co/Mg = 1.0)
- Co-MgO (Co/Mg = 0 to ∞)
- Ni and/or cobalt containing alkaline earth oxide (viz., CaO, SrO, MgO) and mixed alkaline earth oxide (MgO-CaO, MgO-SrO, MgO-BaO, CaO-SrO, CaO-BaO, and SrO-BaO with alkaline earth mole ratio = 1.0).
- Ni and/or cobalt containing ZrO₂, ThO₂, UO₂, TiO₂, and SiO₂ catalysts.
- Pt-or Pd-containing alkaline (MgO, CaO) and rare earth oxide (viz., La₂O₃, Pr₆O₁₁, Nd₂O₃, Sm₂O₃, Gd₂O₃, Dy₂O₃ and Er₂O₃) catalysts.
- NiO/MgO/SA-5205 catalysts (with Co/Ni = 0 to 1.0)

2) To study the following reactions

- CO₂ reforming over NiO-MgO (Ni/Mg=1.0)and NiO-CoO-MgO (Ni+Co/MgO = 1.0) Co_x Ni_{1-x}O/MgO/SA-5205 (Co/Ni = 0.0-1.0)
- Steam reforming over Co_x Ni_{1-x}O/MgO /SA-5205 (Co/Ni ratio = 0.0-1.0)
- Simultaneous steam and CO₂ reforming over NiO-MgO (Ni/Mg=1.0), NiO-CoO-MgO (Ni+Co/MgO = 1.0) and Co_x Ni_{1-x}O/MgO /SA-5205 (Co/Ni ratio = 0.0-1.0)
- Simultaneous oxidative methane-to-syngas conversion reaction with steam reforming of methane over Co_x Ni_{1-x}O/MgO /SA-5205 (Co/Ni ratio = 0.0-1.0)
- Simultaneous oxidative methane-to-syngas conversion reaction with CO₂ reforming of methane over Co_x Ni_{1-x}O/MgO /SA-5205 (Co/Ni ratio = 0.0-1.0)
- Simultaneous oxidative methane-to-syngas conversion reaction with steam and CO₂ reforming of methane over Co_x Ni_{1-x}O/MgO /SA-5205 (Co/Ni ratio = 0.0-1.0)

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PART-II
EXPERIMENTAL

2. EXPERIMENTAL

2.1 GASES AND CHEMICALS

The following gases and chemicals have been used.

Carbon dioxide	:	High purity (99.99%) obtained from L 'Air Liquide, France.
Helium	:	High purity IOLAR-II Grade (99.99%) obtained from Indian Oxygen Ltd.,Bombay
Hydrogen	:	IOLAR II- Grade obtained from Indian Oxygen Ltd., Bombay
6.0 % H ₂ /Ar Mixt.	:	High purity (99.99%) obtained from
Methane	:	High purity (99.99%) obtained from L 'Air Liquide, France.
Nitrogen	:	IOLAR II- Grade obtained from Indian Oxygen Ltd., Bombay
Oxygen	:	IOLAR II- Grade obtained from Indian Oxygen Ltd., Bombay
Magnesium carbonate	:	GR Grade (Loba-Chemie)
Nickel nitrate	:	GR Grade (Loba-Chemie)
Calcium hydroxide	:	Special (Qualigens, SQ)
Calcium nitrate	:	GR Grade (Loba-Chemie)
Calcium acetate	:	GR Grade (Loba-Chemie)
Calcium oxide	:	LR Grade (S. D. Fine Chemicals)
Cobalt nitrate	:	GR Grade (Loba-Chemie)
Lanthanum oxide	:	Aldrich (99.9%)
Praseodymium oxide	:	Aldrich (99.9%)
Neodymium oxide	:	Aldrich (99.9%)
Samarium oxide	:	Aldrich (99.9%)
Gadolinium oxide	:	Aldrich (99.9%)
Terbium oxide	:	Aldrich (99.9%)
Europium oxide	:	Aldrich (99.9%)
Dysprosium oxide	:	Aldrich (99.9%)
Erbium oxide	:	Aldrich (99.9%)

Ytterbium oxide	:	Aldrich (99.9%)
Pt - Chloride (PtCl ₆)	:	Sisco Lab., Bombay
Pd-Chloride (PdCl ₂)	:	Sisco Lab., Bombay
Zirconia (ZrO ₂)	:	GR Loba (99.9%)
Thoria (ThO ₂)	:	GR Loba (99.9%)
Urania (UO ₂)	:	GR Loba (99.9%)
Titania (TiO ₂)	:	GR Loba (99.9%)
Silica (SiO ₂)	:	Fuji-Division, Adsorbent Grade, (B type)
Hydrochloric acid	:	S. D. Chemicals (GR Grade)
Barium nitrate	:	S.D. (L.R.)
Strontium nitrate	:	GR Loba (99.9%)
Chloroplatinic acid (H ₂ PtCl ₆ . ZH ₂ O) ₂	:	Arora-Mathew (Calcutta)

2.2 CATALYST PREPARATION

2.2.1 NiO-MgO

The NiO-MgO catalysts with different Ni/Mg mole ratios were prepared from thick paste of thoroughly mixed, finely ground nickel nitrate (GR LOBA), magnesium carbonate (GR LOBA), and deionized water, which was dried and heated in air at 600°C for 4h. The treated solid was powdered, pressed without a binding agent, crushed to particles of 22-30 mesh, and calcined in air at 900°C for 6h.

2.2.2 CoO-MgO

The CoO-MgO catalysts with different Co/Mg mole ratios were prepared by thoroughly mixing finely ground pure magnesium carbonate and cobalt nitrate, in desired proportions, with deionized water sufficient to form thick paste, drying and decomposing in air at 600°C for 4h. Then the resulting mass was powdered, pressed binder free, crushed to 22-30 mesh size particles and calcined in air at 900°C for 4h.

2.2.3 NiO-CoO-MgO

The NiO-CoO-MgO catalyst with [(Ni+Co)/Mg = 1.0 and Ni/Co = 1.0] was prepared by thoroughly mixing finely ground pure magnesium carbonate and cobalt nitrate and nickel nitrate, in desired proportions, with deionized water, sufficient to form a thick paste, drying and decomposing in air at 600°C for 4h. The resulting mass was powdered, pressed binder free, crushed to 22-30 mesh size particles and calcined in air at 900°C for 4h.

2.2.4 Ni-containing Alkaline Earth oxide Catalysts

The NiO-alkaline earth oxide(s) (viz., MgO-CaO, MgO-SrO, MgO-BaO, CaO-SrO, CaO-BaO and SrO-BaO) catalysts 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 4h, powdering, pressing and crushing to 30-60 mesh particles and calcining in air at 930°C for 4h. 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.

2.2.5 Pd or Pt (1.0 wt%) containing Alkaline and Rare Earth Oxides Catalysts

The Pd or Pt (1.0 wt%) containing alkaline earth oxides (viz. MgO or CaO) or rare earth oxide (viz. La₂O₃, Pr₆O₁₁, Nd₂O₃, Sm₂O₃, Gd₂O₃, Dy₂O₃ and Er₂O₃) catalysts were prepared by impregnating the corresponding alkaline or rare earth oxide with aqueous Pd or Pt chloride by incipient wetness technique, drying at 120°C for 16 h, decomposing at 600°C for 4 h under static air, powdering and pressing binder-free, crushing to 22-30 mesh size particles and calcimining at 900°C for 6h in air.

2.2.6 Ni-containing Mixed Metal Oxide Catalysts

The nickel containing mixed metal oxide catalysts (with Ni/MO₂ mole ratio of 1.0, where M=Zr, Th, U, Ti or Si) were prepared by thoroughly mixing powdered nickel nitrate (GR Loba) with zirconyl nitrate (GR LOBA) or uranyl nitrate (GR LOBA) or

thorium nitrate (GR Loba), TiO_2 (GR LOBA) or silica gel (Fuji-Division, adsorbent grade, B- type) along with demonized water sufficient to form thick paste, drying and decomposing in air at 600°C for 4h and then powdering, pressing binder-free, crushing to particles of 22-30 mesh size and calcining at 900°C for 4h. The Co and Ni-Co containing ZrO_2 , ThO_2 and UO_2 catalysts were prepared by the same procedure using Co-nitrate or mixed Ni-and Co-nitrates (Ni/Co=1.0) instead of Ni-nitrate.

2.2.7 NiO/MgO/SA-5205

Supported nickel catalyst [NiO (13.6 wt.)/MgO (5.1 wt.)/SA-5205] used in this investigation was developed in our laboratory for the partial oxidation of methane to syngas at extremely short (≈ 1 ms) contact times. It has high thermal and hydrothermal stability and also has high mechanical strength. It was prepared by depositing nickel nitrate from its aqueous solution on 22-30 mesh size particles of commercial catalyst carrier - SA-5205 [sintered low surface area macroporous silica support support, obtained from Norton Co., USA] precoated with MgO, using an incipient wetness impregnation technique followed by drying and decomposing (or calcining) in air at 900°C for 4h. The catalyst carrier was precoated with MgO by impregnating the carrier with Mg-nitrate, drying and decomposing as above. The support consists mainly of alumina (86.1 wt.%) and silica (11.8 wt.%) and its surface area, porosity, pore volume and average pore size are $< 0.01 \text{ m}^2 \cdot \text{g}^{-1}$, 54 %, $0.35 \text{ cm}^3 \cdot \text{g}^{-1}$ and $200 \mu\text{m}$, respectively.

2.2.8 NiO-CoO/MgO/SA-5205

Supported $\text{Co}_x\text{Ni}_{1-x}\text{O}$ (14.0 ± 0.5 wt%)/MgO/SA-5205 ($x = 0.05, 0.15, 0.29, \text{ and } 0.5$) catalysts (Table 1) were prepared by depositing mixed nitrates of Ni and Co with desired Co/Ni ratio (0.05, 0.17, 0.4, or 1.0) from their aqueous solution on 22-30 mesh size particles of commercial catalyst carrier, SA-5205 [sintered low surface area macroporous silica support, obtained from M/S Norton Co. USA] precoated with MgO, using an incipient wetness impregnating technique, followed by drying and decomposing(or calcining) in air at 900°C for 4h. The catalyst carrier was precoated with MgO by impregnating the carrier with Mg-nitrate, drying and decomposing as above. The support

consists mainly of alumina (86.1%) and silica (11.8 wt%) and its surface area, porosity, pore volume and average pore size are $<0.01 \text{ m}^2 \text{ g}^{-1}$, 54%, $0.35 \text{ cm}^3 \text{ g}^{-1}$ and $200 \text{ }\mu\text{m}$, respectively.

2.3 CATALYST CHARACTERIZATION

2.3.1. Surface Area

The surface area of the catalysts was measured by single-point BET method by measuring the adsorption of nitrogen at liquid temperature and at N_2 concentration of 30 mol % (balance helium), using a Monosorb Surface Area Analyzer (Quanta Chrome Corp., USA) based on dynamic adsorption/desorption technique.

Before carrying out surface area measurement experiments, the catalyst (0.5-2.0) was pretreated insitu in the sample cell at 300°C for 1h in flow ($30 \text{ cm}^3 \text{ min}^{-1}$) of a mixture of helium and nitrogen to remove the traces of moisture and also the analyzer was calibrated by injecting a known amount of air.

The surface area was calculated from the observed desorption counts instead of the adsorption ones, as follows:

$$\text{Surface area (m}^2 \text{ g}^{-1}\text{)} = \frac{\text{Desorption counts} \times 2.84}{\text{Wt. of catalyst} \times \text{counts of 1 ml of air}}$$

($2.84 \text{ m}^2 \text{ area} = 1 \text{ cm}^3$ of N_2 or air, counts are expressed in terms of surface area, m^2)

2.3.2. Coke/Carbon Estimation by Micro-analysis

The carbon deposited on the catalysts was determined by its complete and instantaneous oxidation by flash combustion using Carlo Erba Analyzer Model EA 1108. .

2.3.3. X-Ray Diffraction (XRD)

The XRD analysis of the catalysts used in the oxidative conversion of methane to synthesis gas reactions was done by the X-ray powder diffraction method using a Holland Phillips, PW/1730 X-ray generator with CuK radiation scintillation counter.

2.3.4 XPS (ESCA)

Surface chemical analysis of the catalyst was done by the X-ray photoelectron spectroscopy (XPS) using a VG- scientific ESCA-3 MK II electron spectrometer (C1s with binding energy = 285 eV was used as internal standard) Before these measurements, the catalyst was pretreated at 900°C for 1h in a flow of moisture-free N₂ and it was used with minimum exposure to atmospheric moisture and CO₂.

The surface concentration of the elements present in the reduced and fresh catalysts has estimated as follows,

$$\frac{\text{Area under curve} \times \text{scale}}{\text{Cross-sectional area of an element} \times \text{Magnitude}}$$

2.3.5 Temperature Programmed Reduction with H₂

The schematic diagram of the experimental set-up used for the measurement of temperature programmed reduction with H₂ of the catalysts is shown in Figures 2.3.1 2.3.2. The temperature programmed reduction (TPR) of the unreduced catalysts was carried out in a quartz reactor (I.D. 4.5 mm), packed with .05 g catalyst) in a flow (60 cm³ min⁻¹) of H₂-Ar mixture (2.0 mol% H₂) from 100°-900°C at a linear heating rate of 10°C min⁻¹. The hydrogen consumed in the TPR was measured quantitatively by TCD. Before carrying out the temperature programmed reaction with methane or reduction by H₂ , the catalyst was pretreated insitu at 900°C for 1h in a flow of moisture-free helium (50 cm³ min⁻¹).

2.3.6 Temperature Programmed Reaction with CH₄

The experimental set-up used to study the temperature programmed reaction with CH₄ is shown in Figure 2.3.6

The temperature programmed reaction of methane (in the absence of free-oxygen) over the unreduced catalysts was carried out in a quartz reactor (i.d.=10mm) by passing a mixture of methane and helium (5.0 mol% CH₄) at a flow rate of 100 cm³ min⁻¹ over 0.3 g

Catalyst Pretreatment Mode

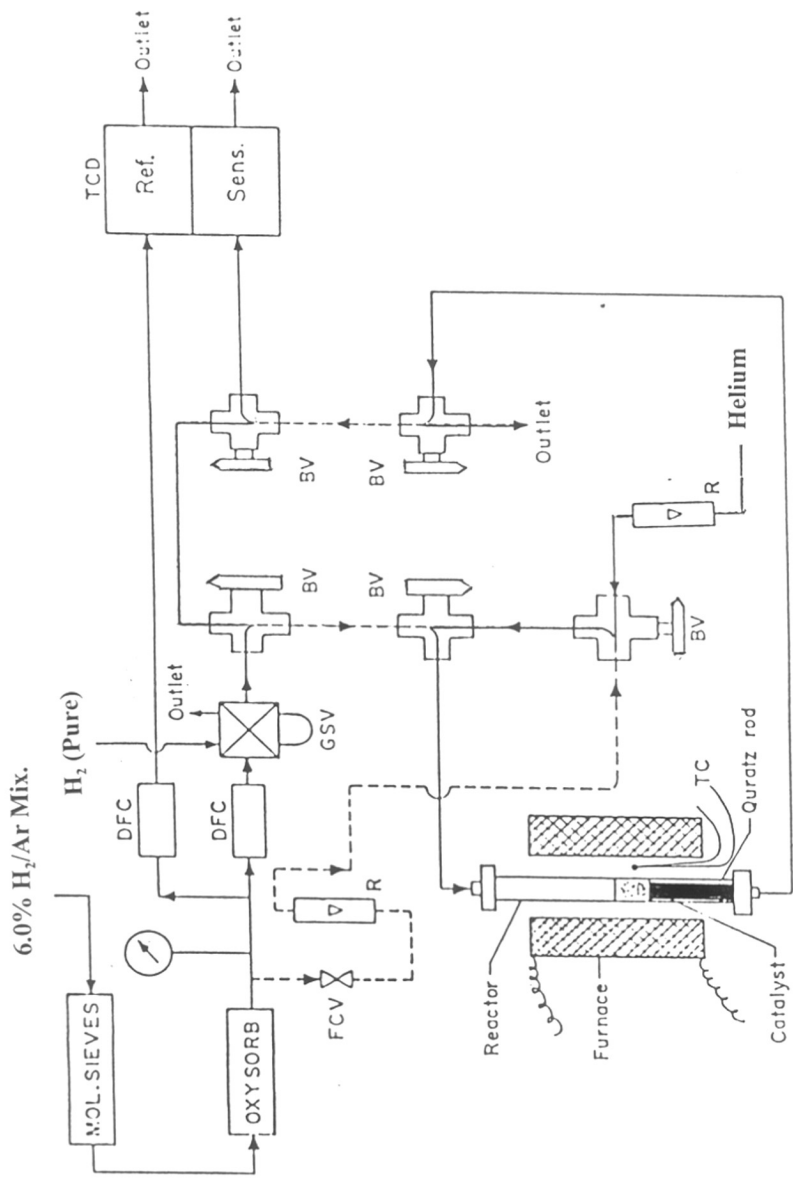


Fig. 2.3.1: Schematic Diagram for Temperature Programmed Reduction (TPR) with H₂

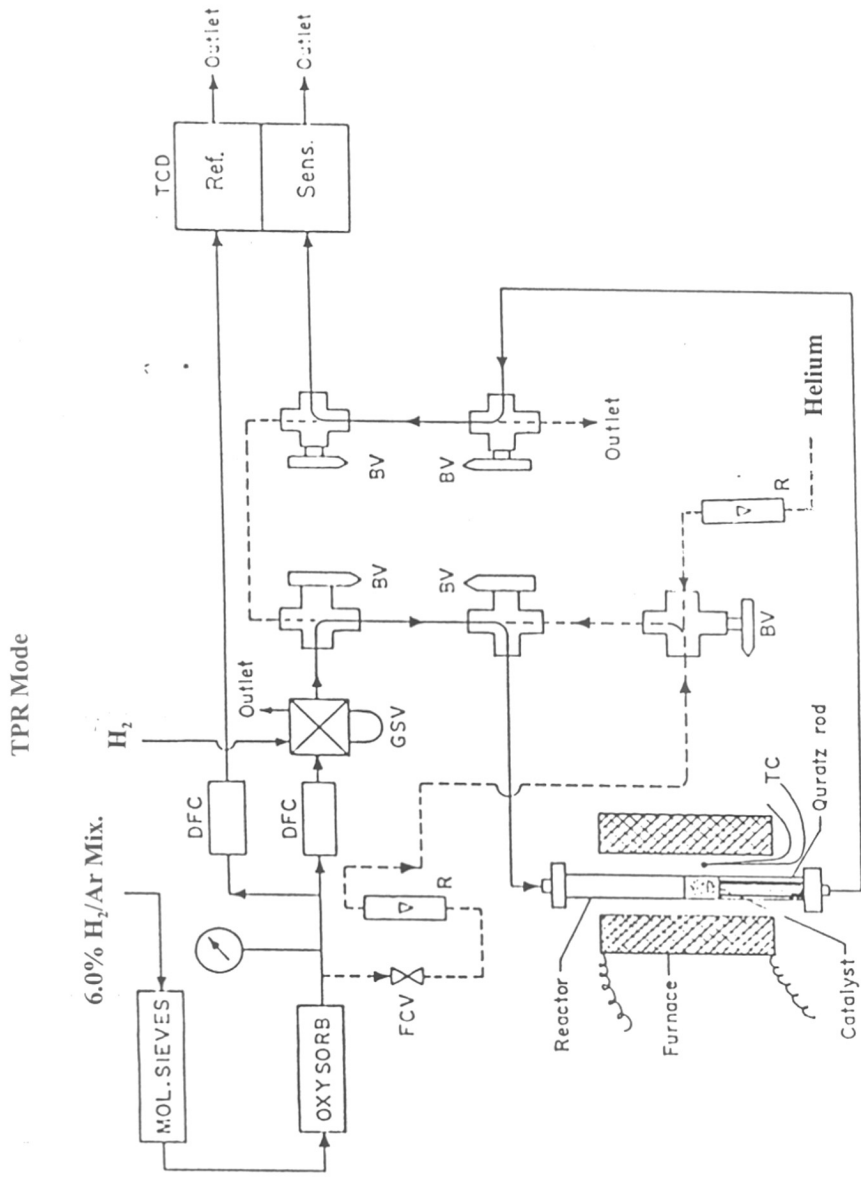


Fig. 2.3.2: Schematic Diagram for Temperature Programmed Reduction (TPR) with H₂

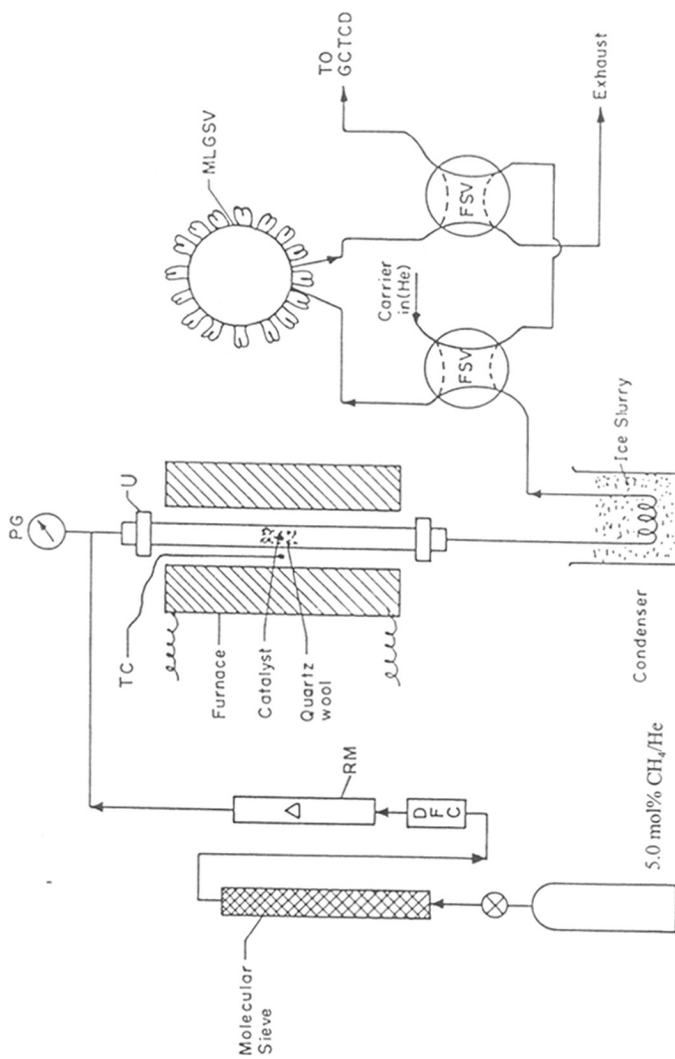


Fig. 2.3.6: Schematic Diagram for Temperature Programmed Reaction with CH_4

unreduced catalyst from 100° to 900°C at a linear heating rate of 20°C min⁻¹. The reaction products were sampled at different temperatures, using a sixteen-loop gas sampling valve and analyzed by GC using a Spherocarb column.

2.3.7 Hydrogen Chemisorption

The hydrogen chemisorption uptake on the catalysts was obtained by pulse chemisorption technique using H₂ pulse at 40°C for Pt-containing catalysts and using diluted H₂ (6.0 % H₂ in Argon) pulses for Pd-containing catalysts after reducing them insitu with H₂ at 350°C for 1h. The pulse micro-reactor, operating in the catalyst and in the chemisorption modes is shown in Figs. 2.3.3-5.

2.4 CATALYTIC REACTIONS

2.4.1 Oxidative Conversion of Methane to Syngas

The experimental setup and quartz reactor used for the partial oxidation of methane to syngas are shown in Figs. 2.4.1 and 2.4.3

The oxidative methane-to-syngas conversion over the catalyst (20 mg) was carried out in a continuous flow microreactor (i.d. 4mm) made up of quartz at 1 atm using a feed consisting of pure methane (64 mol%) and oxygen (36 mol%) with CH₄/O₂ ratio of about 1.8 and total space velocity (measured). The reaction temperature was measured with Chromel-Alumel thermocouple located in catalyst bed. The water from the reaction product was separated by condensing at 0°C. The feed and product were analyzed by an on-line GC equipped with TCD using Spherocarb column at the following GC operating conditions:

Detector temperature	:	100°C
Injector temperature	:	100°C
Oven temperature	:	45°C
Current	:	132 mA
He-carrier gas flow rate	:	35 cm ³ min ⁻¹

Catalyst Pretreatment Mode

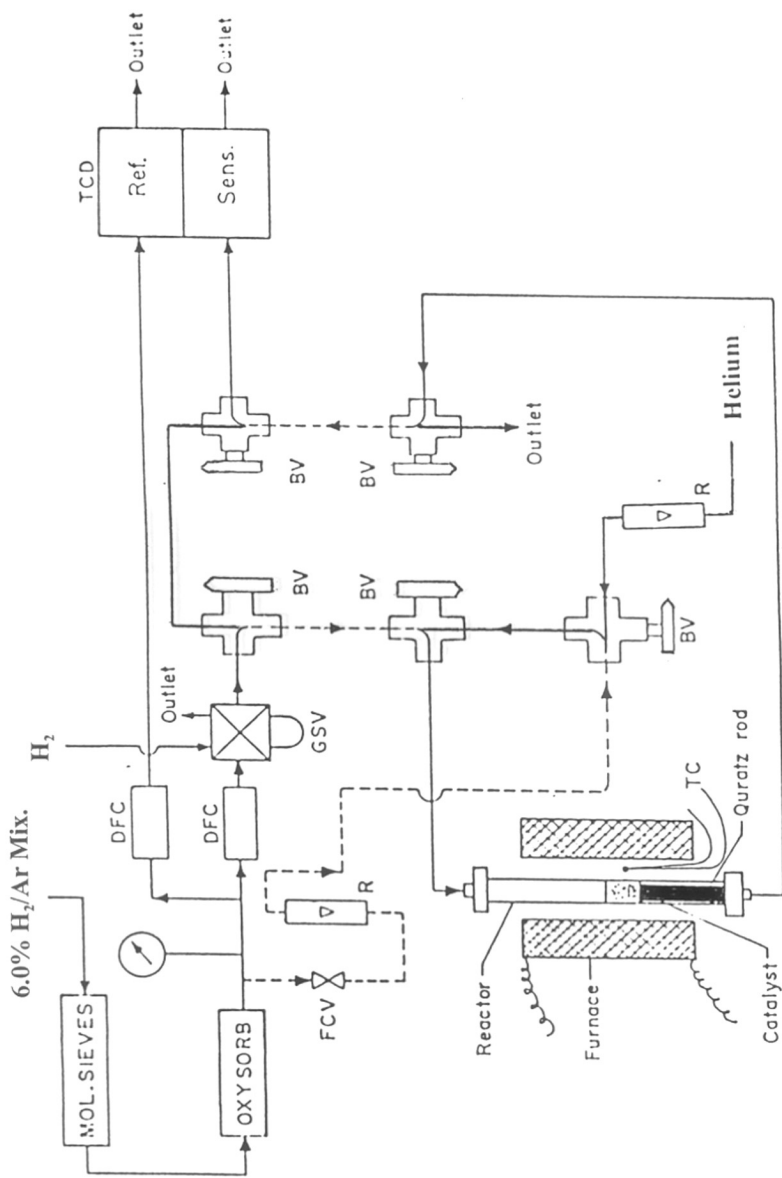


Fig. 2.3.3: Schematic Diagram for Hydrogen Chemisorption

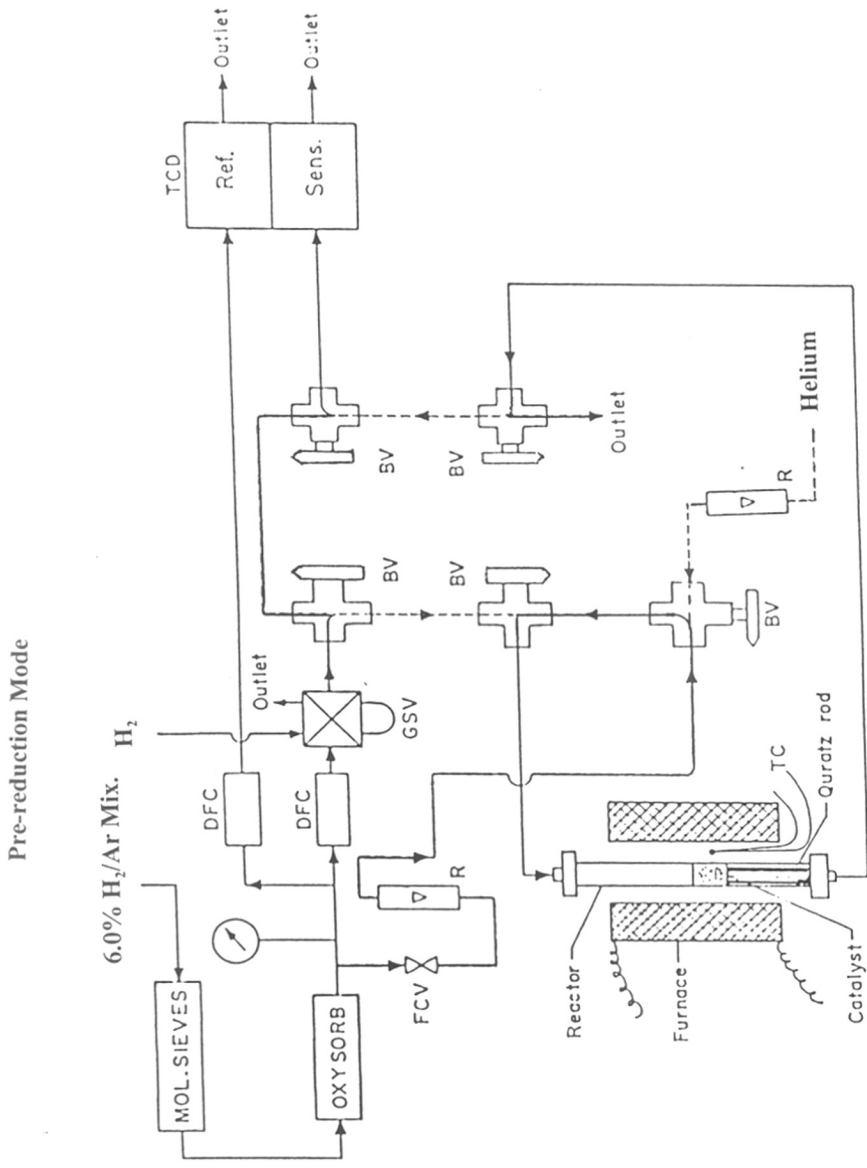


Fig. 2.3.4: Schematic Diagram for Hydrogen Chemisorption

H₂ Pulse Mode

6.0% H₂/Ar Mix.

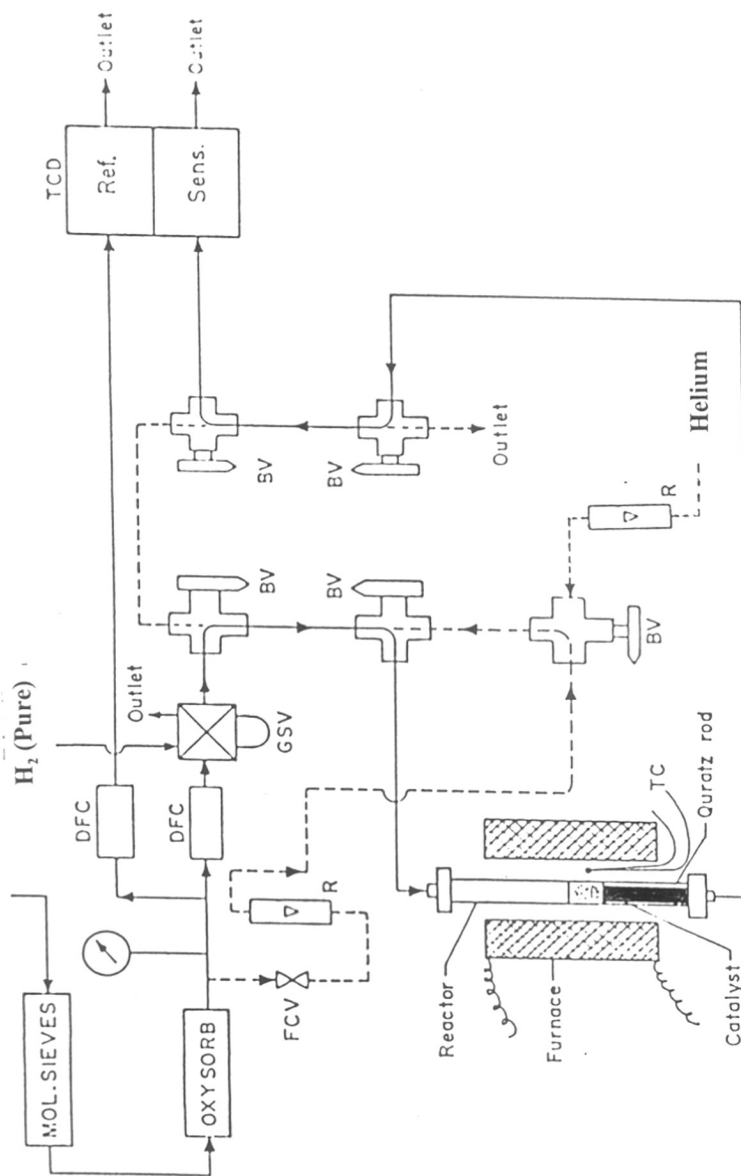


Fig. 2.3.5: Schematic Diagram for Hydrogen Chemisorption

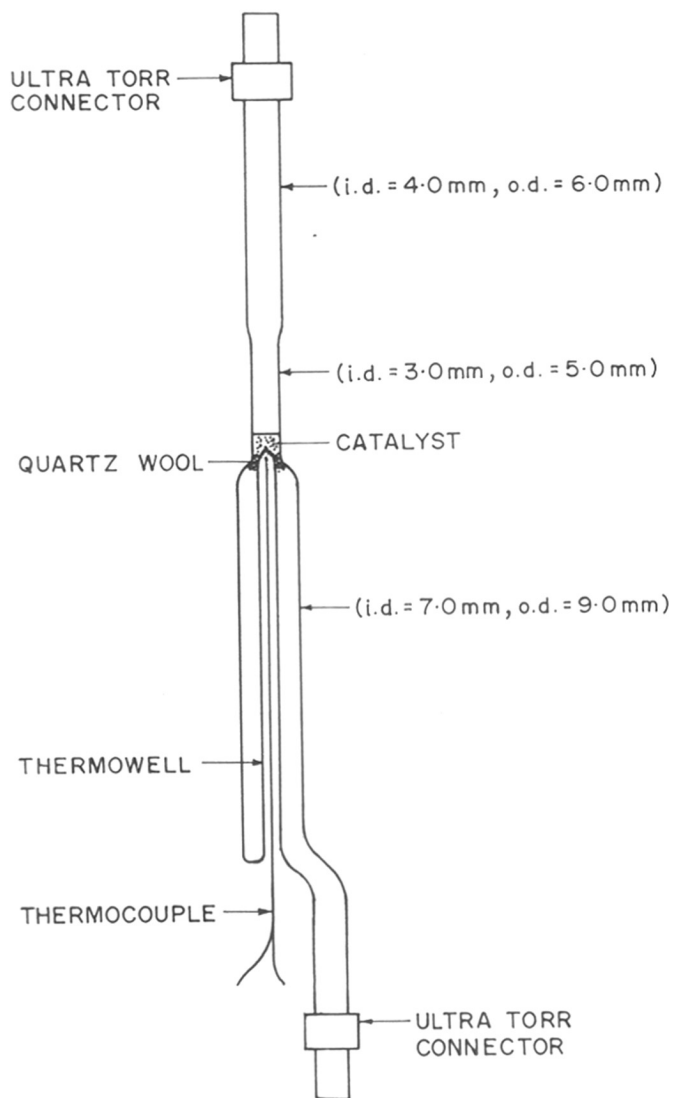


Fig. 2.4.1: Quartz Flow Reactor for Oxidative Conversion of Methane to Syngas

The response factor and retention time of the product gases were obtained by injecting the high purity individual gases into the column before carrying out the methane-to-syngas conversion reaction.

The methane conversion, CO-selectivity, H₂-selectivity, GHSV (gas hourly space velocity) and CO-productivity are defined/calculated as follows:

$$\text{Conversion, \%} = \frac{\text{Reactant}|_{\text{Feed}} - \text{Reactant}|_{\text{product}}}{\text{Reactant}|_{\text{Feed}}} \times 100$$

$$\text{Selectivity, \%} = \frac{\text{Conversion of reactant to a particular product}}{\text{Conversion of reactant}} \times 100$$

$$\text{GHSV (cm}^3 \text{ g}^{-1} \text{ h}^{-1}\text{)} = \frac{\text{Total flow rate of feed gases (at } ^\circ\text{C and 1 atm.) (cm}^3 \text{ h}^{-1}\text{)}}{\text{wt. of catalyst (g)}}$$

$$\text{CO productivity (mol g}^{-1} \text{ h}^{-1}\text{)} = \frac{\text{GHSV} \times \text{FC of CH}_4 \times \text{MF of CH}_4 \times \text{FS of CO}}{22400}$$

where, FC = Fractional conversion

MF = Mole fraction

FS = Fractional selectivity

2.4.2 Steam and/or CO₂ Reforming of Methane

The experimental setup and quartz reactor used for the catalytic steam and/or CO₂ reforming of methane of methane to syngas are shown in Figs.2.4.3 and 2.4.2, respectively.

The catalytic steam and/or CO₂ reforming of methane-to-syngas reactions over the catalysts were carried out at the atmospheric pressure in a continuous flow quartz reactor (i.d. 9 mm) packed with 0.3 g catalyst and provided with a chromel-alumel thermocouple located in the center of the catalyst bed. The feed was a mixture of pure methane (> 99.95 %), CO₂ (99.99 %) and/or steam. Water was added to the feed using a SAGE syringe pump and a specially designed evaporator. Before carrying out the reaction, the catalyst

was heated insitu at 900°C in a flow ($50 \text{ cm}^3 \cdot \text{min}^{-1}$) of moisture-free nitrogen for 1h. The catalytic reactions were carried out at different temperatures, gas hourly space velocities (GHSV, measured at 0°C at 1 atm) and relative concentrations of methane, steam, CO_2 in the feed. The product gases (after condensation of the water from them at 0°C) were analyzed by an on-line gas chromatography with TCD, using a Sphero carb column and He as a carrier gas. The conversion/selectivity data were collected after a reaction period of 30 min.

2.4.3 Simultaneous Oxidative Conversion and Steam and /or CO_2 Reforming of Methane

The experimental setup and quartz reactor used for the oxy- CO_2 reforming, oxy-steam reforming, and oxy- CO_2 and steam reforming of methane-to-syngas reactions are shown in Figs. 2.4.3 and 2.4.2, respectively.

The catalytic oxy- CO_2 reforming, oxy-steam reforming, and oxy- CO_2 and steam reforming of methane-to-syngas reactions over the catalysts were carried out at atmospheric pressure in a continuous flow quartz reactor (i.d. 9 mm) packed with 0.3 g catalyst and provided with a chromel-alumel thermocouple located in the center of the catalyst bed. The feed was a mixture of pure methane (> 99.95 %), O_2 (99.9%), CO_2 (99.99 %) and/or steam. Water was added to the feed using a SAGE syringe pump and a specially designed evaporator. Before carrying out the reaction, the catalyst was heated insitu at 900°C in a flow ($50 \text{ cm}^3 \text{ min}^{-1}$) of moisture-free nitrogen for 1h. The catalytic reactions were carried out at different temperatures, gas hourly space velocities (GHSV), (measured at 0°C at 1 atm) and relative concentrations of methane, O_2 , CO_2 , or steam in the feed. The product gases (after condensation of the water from them at 0°C) were analyzed by an on-line gas chromatography with TCD, using a Sphero carb column and He as a carrier gas. The C, H, and O balances across the reactor was within 2-6%. All experiments with larger error in the material balances were rejected.

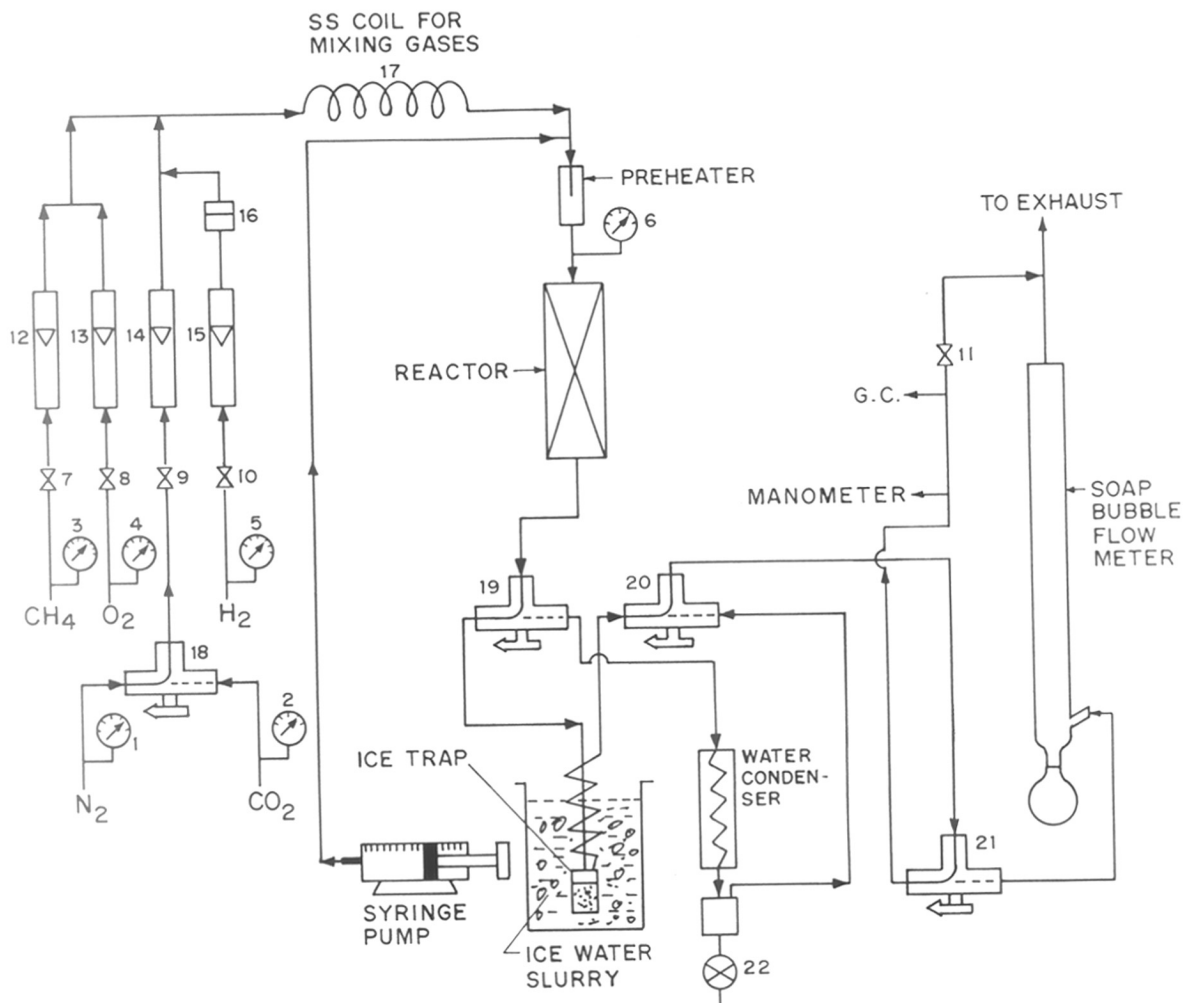


Fig.2.4.3: Experimental Setup for Evaluation of Catalyst Performance in Oxidative Conversion of Methane, oxy- CO_2 Reforming, oxy-steam Reforming, CO_2 -steam Reforming and Simultaneous oxy- CO_2 and Steam Reforming of Methane to Syngas

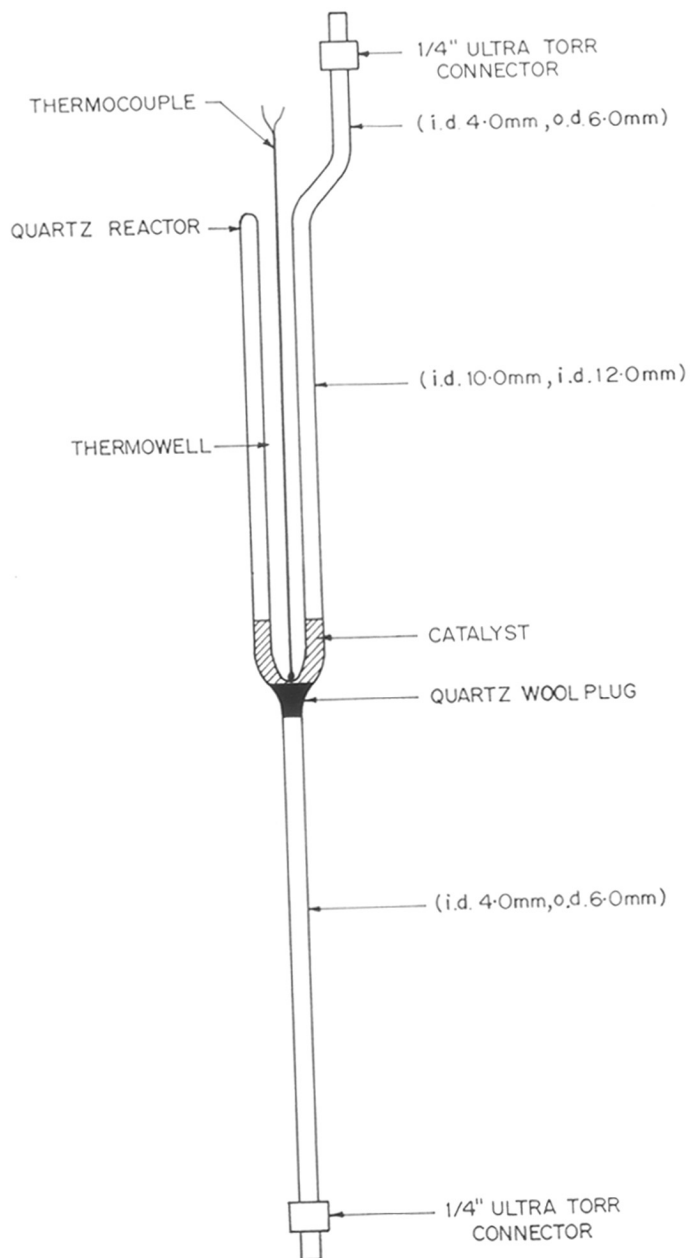


Fig. 2.4.2: Quartz Flow Reactor Used for Methane-to-Syngas Conversion Reactions

PART-III

CATALYTIC PARTIAL OXIDATION OF METHANE TO SYNGAS

CHAPTER-3.1

NiO-ALKALINE EARTH OXIDE(S) CATALYSTS FOR OXIDATIVE METHANE-TO-SYNGAS CONVERSION: INFLUENCE OF ALKALINE EARTH OXIDE ON THE SURFACE PROPERTIES AND TEMPERATURE PROGRAMMED REDUCTION/REACTION BY H₂ AND METHANE

3.1.1 EARLIER LITERATURE AND OBJECTIVES OF THIS WORK

NiO-MgO (1-5) and NiO-CaO (2, 6-10) catalysts show high activity/selectivity in the methane-to-syngas (CO and H₂) conversion reaction involving partial oxidation of methane (1-3), steam reforming and/or CO₂ 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 catalysts is reduced to its metallic form (Ni⁰) 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 CO₂ 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 H₂ and surface properties.

The present investigation was undertaken with the objective of comparing the different NiO alkaline earth oxide and mixed alkaline earth oxides catalysts (calcined at 930°C) for their (i) temperature programmed reaction with pure methane (in the absence of free O₂) from 100° to 900°C, (ii) temperature programmed reduction by H₂ 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).

3.1.2 RESULTS

3.1.2.1 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 H₂ of the NiO-alkaline earth oxide(s) catalysts (reduced before the reaction by H₂ at 500°C and also at 900°C) in the oxidative conversion of methane to syngas (at 700°C) are presented in Table 3.3.1. Among the catalysts, the NiO-MgO, NiO-CaO, NiO-MgO-CaO show high methane conversion and also high selectivity for both H₂ 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.

3.1.2.2 Temperature Programmed Reaction of Methane in the Absence of Free-O₂

Results of the temperature programmed reaction of methane in absence of free -O₂ over the unreduced catalysts from 100°C to 900°C are presented in Figs. 3.1.1-3.1.3. It is interesting to note that the trends for the conversion of methane (by its reaction with the lattice oxygen of NiO producing CO, CO₂, H₂O and/or its dissociation on Ni⁰ produced in the gas solid reaction) - to total and to CO, CO₂ and adsorbed carbon species, vary from catalyst to catalyst. From the results (Figs. 3.1.1-3.1.3), 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 at higher temperatures.
- 2) The methane conversion reaction over the CaO catalyst is much faster at lower temperatures. However, the addition to this catalyst of SrO or BaO results in a decrease in the methane

Table : 3.1.1 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 ₄ conversion (%)	Selectivity (%)			H ₂ /CO mole ratio	CO Productivity (mol.g. ⁻¹ .h. ⁻¹)
		H ₂	CO	CO ₂		
<u>Catalyst reduced at 500°C</u>						
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					
<u>Catalyst reduced at 900°C</u>						
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					

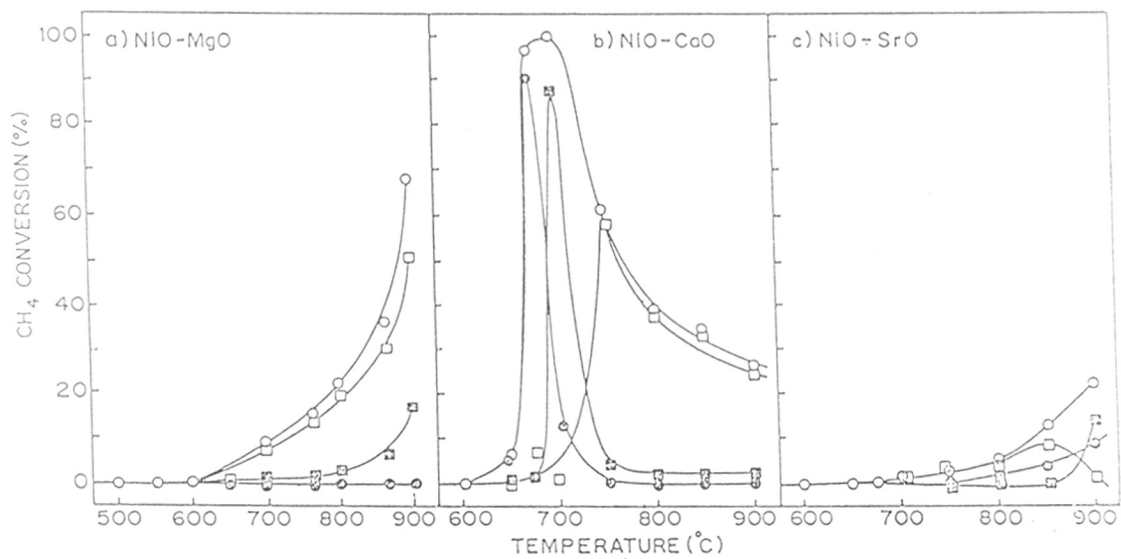


Fig.3.1.1: Temperature programmed reaction of methane with NiO-MgO, NiO-CaO and NiO-SrO catalysts in the absence of free-O₂. [conversion of methane- total (O), to CO₂ (●), to CO (■) and to adsorbed carbon species (□)]

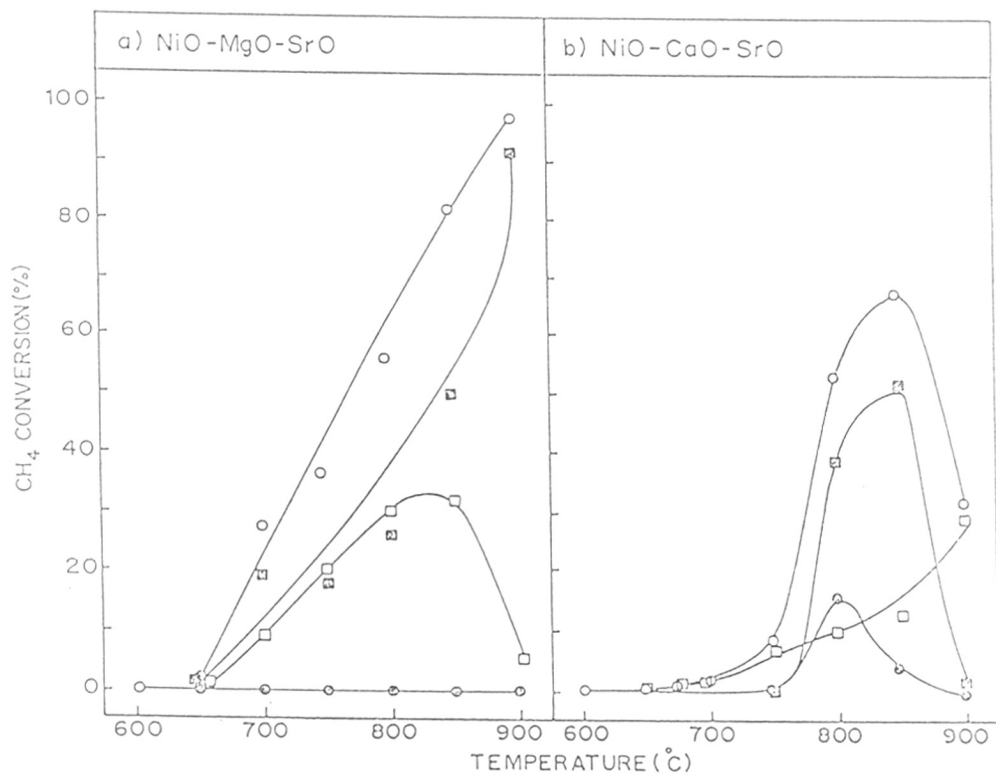


Fig.3.1.2.:Temperature programmed reaction of methane with NiO-MgO-SrO and NiO-CaO-SrO catalysts in the absence of free-O₂. [conversion of methane- total (O), to CO₂ (●), to CO (■) and to adsorbed carbon species (□)]

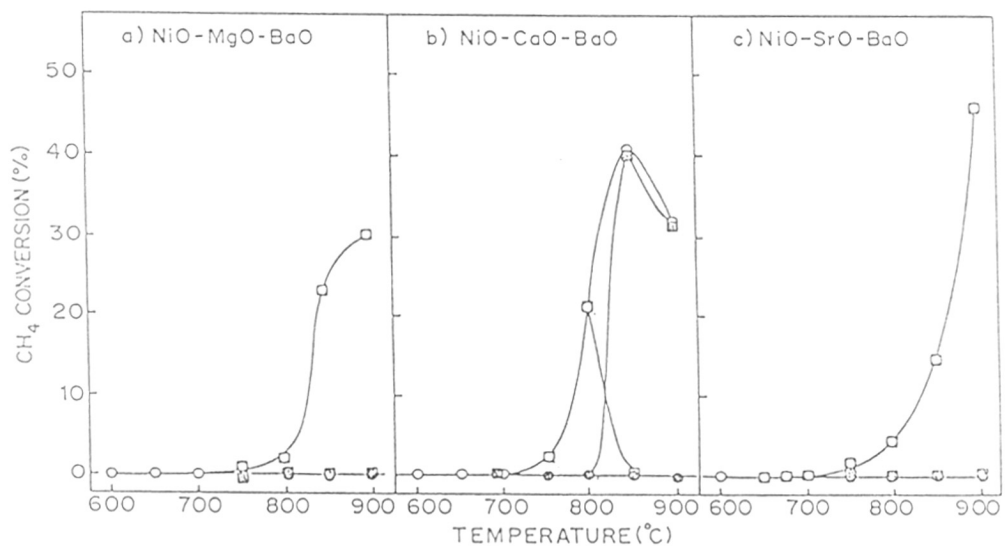


Fig.3.1.3.:Temperature programmed reaction of methane with NiO-MgO-BaO, NiO-CaO-BaO and NiO-SrO-BaO catalysts in the absence of free-O₂. [conversion of methane-total (O), to CO₂ (●), to CO (■) and to adsorbed carbons species (□)]

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 CO₂ 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 CO₂ is detected in the product stream.

3.1.2.3 Temperature Programmed Reduction by H₂

Curves for the temperature programmed reduction (TPR) by H₂ 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. 3.1.4-3.1.6. The data on the TPR peak maximum temperatures of the catalysts along with their surface area are provided in Table 3.1.2.

Table:3.1.2 Surface area and TPR peak maximum temperatures for the NiO-containing alkaline earth metal oxide(s) catalysts (Ni/alkaline earth(s) = 1.0)

catalyst	Surface area (m ² . g ⁻¹)	Peak maximum temperature (°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)	≥ 900 (minor)
NiO-MgO-BaO	0.8	525 (major)	850 (minor)
NiO-SrO-BaO	0.3	450 (minor)	570 (major)

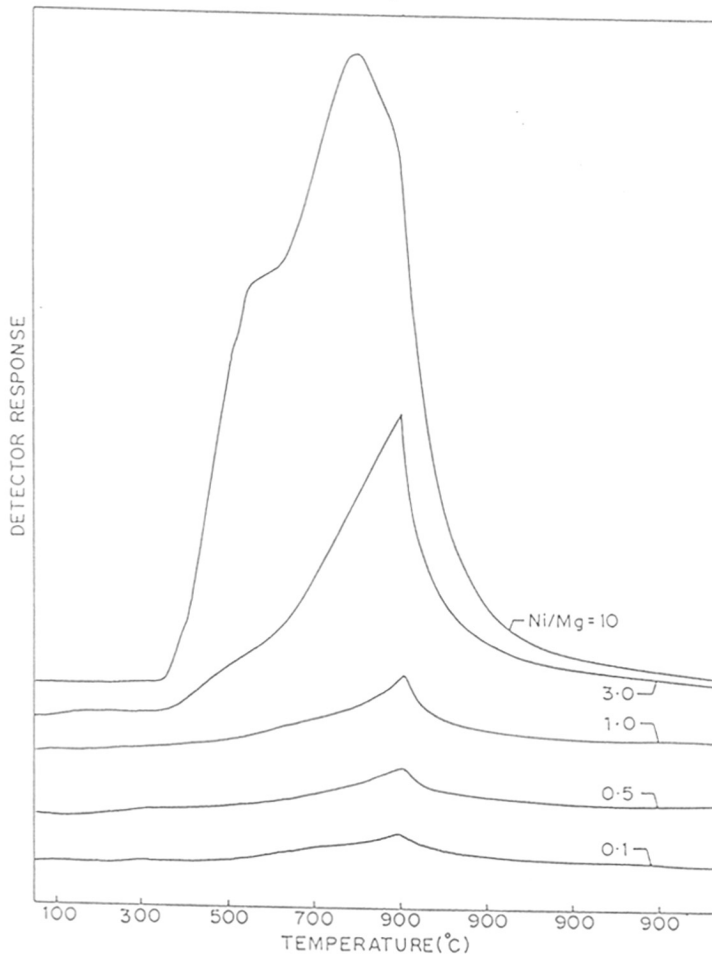


Fig.3.1.4.:Temperature programmed reduction by H_2 of NiO-MgO with different Ni/Mg ratios.

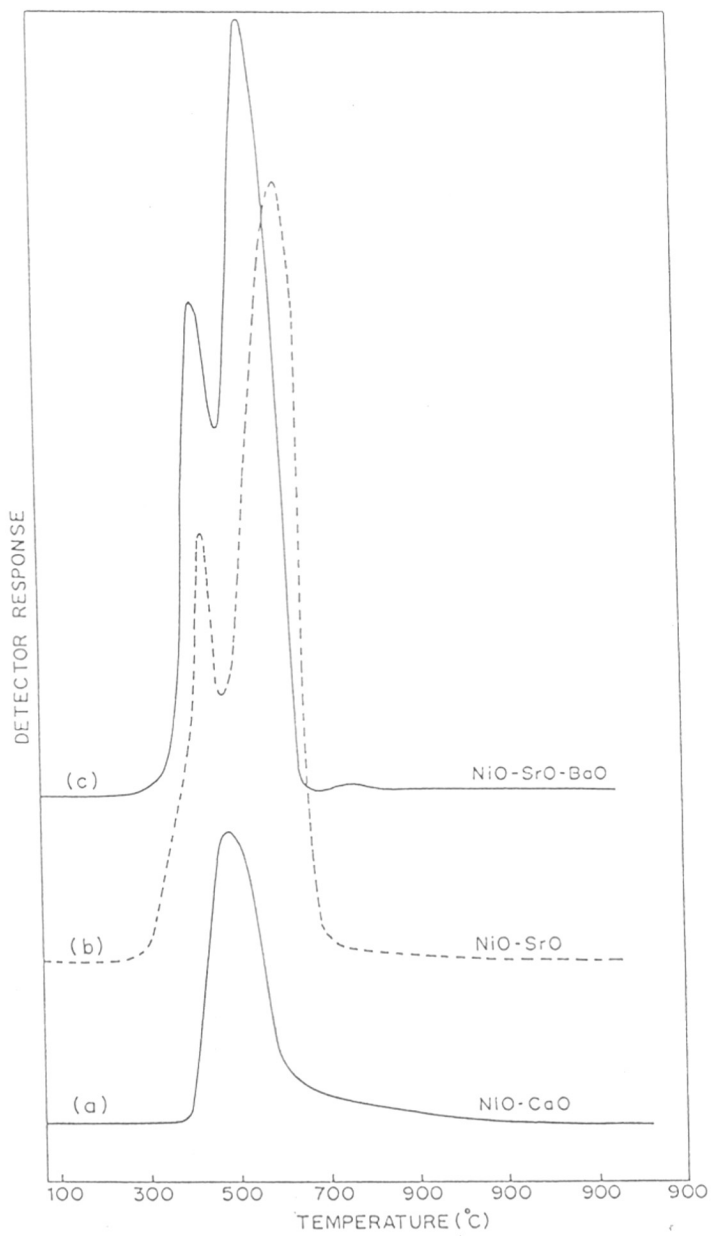


Fig.3.1.5.:Temperature programmed reduction by H_2 of NiO-CaO, NiO-SrO and NiO-SrO-BaO catalysts.

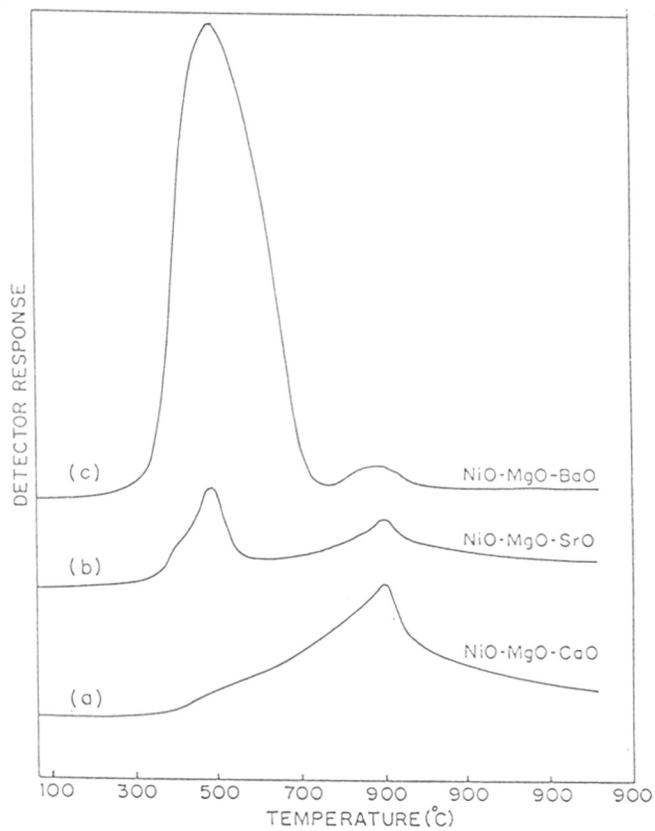


Fig.3.1.6.:Temperature programmed reduction by H_2 of NiO-MgO-CaO, NiO-MgO-BaO and NiO-MgO-SrO catalysts.

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.3.1.4). The TPR peak maximum temperature 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 two peak maxima, as shown in Figs. 3.1.5 & 3.1.6, 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) than that for those containing alkaline earth oxide(s) other than MgO (Table 3.1.2).

Data on the degree of reduction of the NiO from the catalysts in their TPR experiment (i.e. after their reduction by H₂ at 900°C) are given in Table 3.1.3.

Table 3.1.3: Degree of reduction of the NiO from Ni- containing alkaline earth oxide catalysts in their temperature programmed reduction.

Catalyst	Amount of hydrogen consumed (mmol. 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 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, 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 of a particular alkaline earth oxide in the catalyst (Table 3.1.2). 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.

3.1.2.4 Characterization of Reduced Catalysts by XRD and XPS

The NiO-alkaline earth oxide(s) catalysts are reduced by H₂ (30% H₂ in N₂) at 500°C for 1h, passivated by treating them with O₂ (1 mol% O₂ in N₂) at room temperature and then characterized by XRD for their NiO and Ni⁰ phases and by XPS for their surface concentration of nickel and alkaline earth(s).

The XRD spectra (for $2\theta = 42^\circ$ - 46°) of the reduced catalysts are compared with that of the unreduced catalysts in Fig.3.1.7. All the reduced catalysts show the presence of metallic Ni (Ni⁰) (XRD peak at $2\theta = 44.3 \pm 0.1^\circ$). However, the XRD peak for Ni⁰ 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 3.1.3).

The XPS results in Table 3.1.4 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.

3.1.3 DISCUSSION

The NiO-alkaline earth oxide(s) catalysts, reduced by H₂ at 500°C and 900°C, show their activity in the methane-to-syngas conversion reaction in the following order :

Table 3.1.4 : Surface composition of the Ni-containing alkaline earth oxide catalysts without or with reduction (at 500°C by H₂ for 1h)

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

Table 3.1.4: Continued.....

Catalyst	Reduced or unreduced	Surface composition of Ni and alkaline earth elements	Ni/alkaline earth element(s) (mole ratio)
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

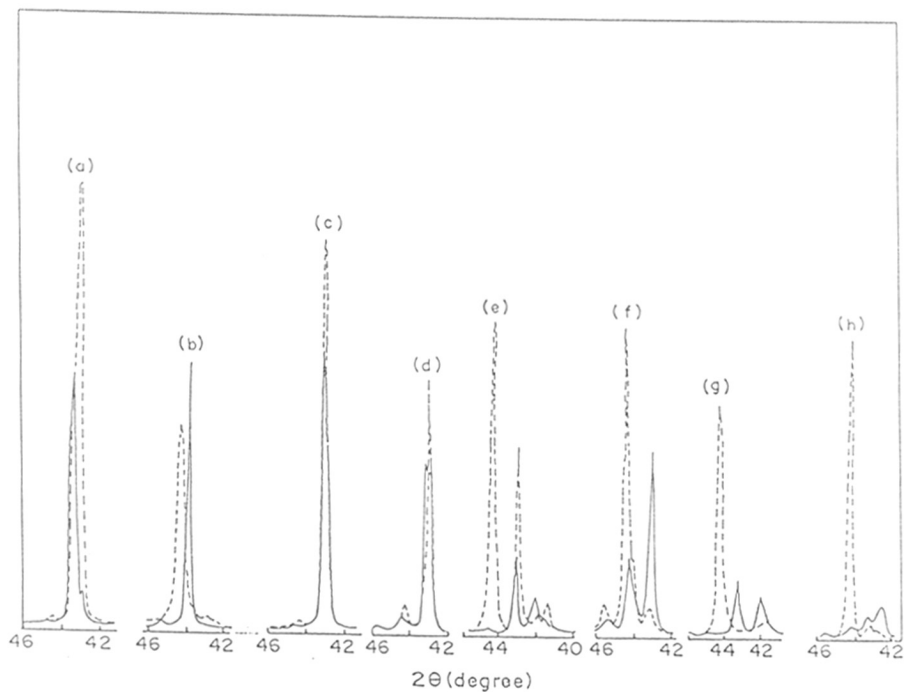
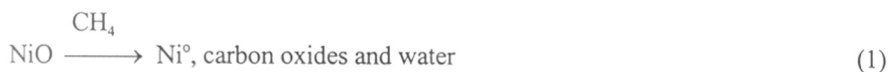


Fig.3.1.7.:XRD spectra for $2\theta = 42-46^\circ$ of the different NiO-alkaline earth oxide(s) catalysts before reduction (—) and after reduction (---) by H_2 at 500°C for 1h. a) NiO-MgO, b) NiO-CaO, c) NiO-MgO-CaO, d) NiO-MgO-SrO, e) NiO-MgO-BaO, f) NiO-CaO-SrO, g) NiO-CaO-BaO, h) NiO-SrO-BaO (Ni^0 and NiO correspond to the peaks at $2\theta = 44.2^\circ$ and 43.6° , respectively).

NiO-MgO (500°C) > NiO-MgO-CaO (500°C) > NiO-CaO (500°C) > NiO-MgO-SrO (900°C) > NiO-MgO-SrO (500°C) > NiO-CaO-SrO (500°C) > NiO-CaO-SrO (900°C) > NiO-SrO (900°C) > NiO-MgO-BaO (900°C) > NiO - SrO (500°C) ≥ NiO-MgO-BaO (500°C) and NiO-CaO-BaO and NiO-SrO-BaO (500°C or 900°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 Ni²⁺ in the MgO matrix forming a solid solution of NiO in MgO. At the high calcination temperature (930°C), a complete solid solution of NiO in MgO is formed (13). In the reduction, the outermost Ni⁰ atoms nucleate to form fine metal particles but some, which lie deeper, remain isolated in the MgO matrix either as Ni⁰ 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 (Ni⁰) 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 lie deeper in the MgO matrix, occurs only at higher temperatures (Figs. 3.1.1a and 3.1.4) and also, the degree of reduction is low (Table 3.1.3) because of the incorporation of Ni²⁺ 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 though the reduction of NiO from NiO-MgO at 500°C is very low (Figs.3.1.4 and 3.1.7), 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.



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 follows :



The CO and CO₂ in the methane conversion reaction are expected to be formed by the reactions of adsorbed carbon or CH_x species with the lattice oxygen.



In the presence of free- O_2 , the conversion of methane to CO and CO_2 over the catalyst is also expected to occur according to the above reactions except the fact that the lattice oxygen ($O_{lattice}$) is replaced by adsorbed oxygen ($O_2 \leftrightarrow 2O_{ad}$) and 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 3.1.1). It also reacts with pure methane yielding CO and/or CO_2 with high conversion even at $\leq 700^\circ C$ (Fig.3.1.1b); the formation of adsorbed carbon species in this case is however observed at the higher temperatures. The maxima observed for the methane conversion (Fig. 3.1.1b) is due to the depletion of the lattice oxygen from the NiO of the catalyst. The reduction of NiO from this catalyst by H_2 (Fig. 3.1.5a) also occurs to an appreciable extent at the lower temperatures (below $600^\circ C$). 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 solid solution of the NiO in CaO, similar to that observed earlier (17). The observed small hump at about $800^\circ C$ in the TPR curve (Fig. 3.1.5a) 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 3.1.1) due to the 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 3.1.3)

The NiO-SrO catalyst reduced at $500^\circ C$ is not active and selective in the process but its performance is improved after the reduction at higher temperature ($900^\circ C$) (Table 3.1.1). 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 ($640^\circ C$) of the major TPR peak (Fig. 3.1.5b) and is also consistent with its reactivity with pure methane to an appreciable extent only at higher temperatures (above $800^\circ C$) (Fig. 3.1.1c). 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 3.1.1) and also in its reaction with pure methane (Figs. 3.1.2a and 3.1.2b). 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 3.1.3) and also an increase in the peak maximum temperature of both the TPR peaks (Table 3.1.2); 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 3.1.1).

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 3.1.3). For these catalysts (except NiO-CaO-BaO), the reactivity of pure methane is low and also there is no formation of CO or CO₂ even at 900°C in their temperature programmed reaction with the methane (Fig. 3.1.3).

The two peak maxima observed in the TPR of SrO and/or BaO containing catalysts (Figs. 3.1.5 and 3.1.6) 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 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. 3.1.6 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 though the SrO and BaO containing catalysts (reduced at 500°C) contain high concentration of metallic nickel (Ni⁰) (Fig. 3.1.7) 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 3.1.1). 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 3.1.4). 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 similar to the decoration effect observed earlier in the case of reduced TiO₂ 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 catalyst during its preparation/calcination is higher when it contains strontium and/or barium compound, as indicated by the observed surface area of the catalysts (Table 3.1.2).

3.1.4 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_2 or reducibility of NiO, surface composition of nickel relative to that of alkaline earth(s) before and after the reduction by H_2 at $500^\circ C$, 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_2 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 $750^\circ C$).
- 5) The surface Ni/alkaline earth(s) ratio for all the catalysts is decreased due to their reduction by H_2 ; 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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CHAPTER-3.2

OXIDATIVE CONVERSION OF METHANE TO SYNGAS OVER NiO-MgO SOLID SOLUTIONS WITH OR WITHOUT CONTAINING COBALT

3.2.1 EARLIER LITERATURE AND OBJECTIVES OF THE PRESENT WORK

At the time of undertaking this work, only a few studies on the selective catalytic oxidation of methane to CO and H₂ over Ln₂Ru₂O₇ (Ln = lanthanide) (1), Eu₂Ir₂O₇, supported transition metal oxides (2) and Ni/Al₂O₃ (3) at 750°C with establishment of thermodynamic equilibrium were reported in the literature. However, although these catalytic processes display high conversion and selectivity at higher temperature (700°C), the CO and/or H₂ selectivity in the oxidation process was very low at low temperatures and equilibrium conditions. The present investigation was undertaken for studying the performance of NiO-MgO solid solutions (Ni/Mg = 0.02-10), with or without containing cobalt in the oxidative conversion of methane to syngas at different process conditions, covering a wide range of process variables particularly at very high space velocity or very low contact times.

3.2.2 RESULTS AND DISCUSSION

3.2.2.1 Oxidative Conversion of Methane-to-Syngas over NiO-MgO Catalysts

Results showing the formation of NiO-MgO solid solution for the NiO-MgO catalysts with different Ni /Mg ratios (0.1-10) are already presented and discussed in the earlier Chapter-3.1.

a) Influence of Ni/Mg ratio

Figure 3.2.1 shows the influence of Ni/Mg ratio on the catalytic activity/selectivity of NiO/MgO catalyst at 500° and at 700°C. The results clearly show that the catalyst with Ni/Mg ratio between 1.0 and 3.0 shows the best performance in this process.

b) Effect of catalyst calcination and reduction temperature

Results in Fig. 3.2.2 show a small but significant effect of the calcination temperature on the performance of the catalyst. Both the methane conversion activity and selectivity for CO and H₂ are increased when the catalyst calcination temperature is increased from 750° to 1200°C. The increase in the catalytic activity and selectivity may be due to the formation of a more and more

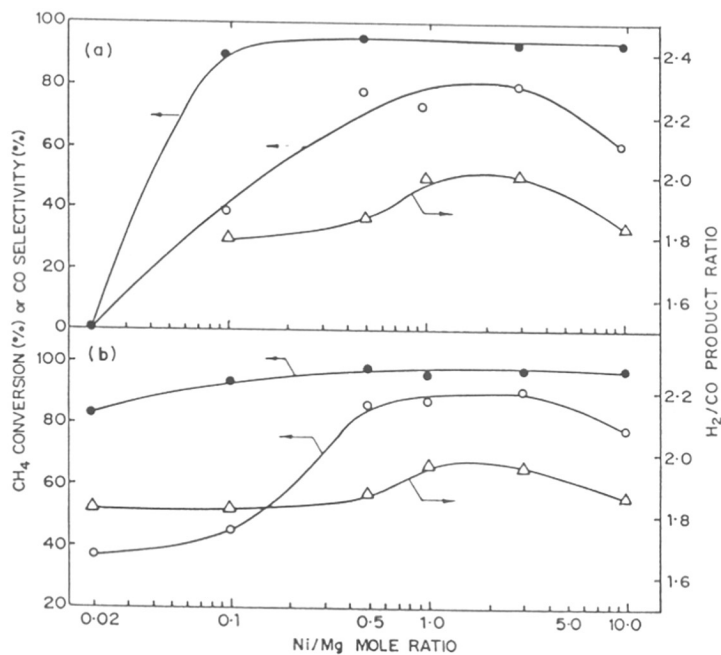


Fig. 3.2.1: Effect of the mol% Ni/Mg on the catalytic activity/selectivity of NiO/MgO at (a) 500°C and (b) 700°C; Feedstock: 67 mol% CH₄ and 33.0 mol% O₂, GHSV = 5.2 × 10⁵ cm³ g⁻¹ h⁻¹). The ordinates on the left correspond to the conversion of methane (O) and the CO selectivity (●) in %. The ordinates on the right correspond to the mol ratio H₂/CO in the product mixture (Δ)

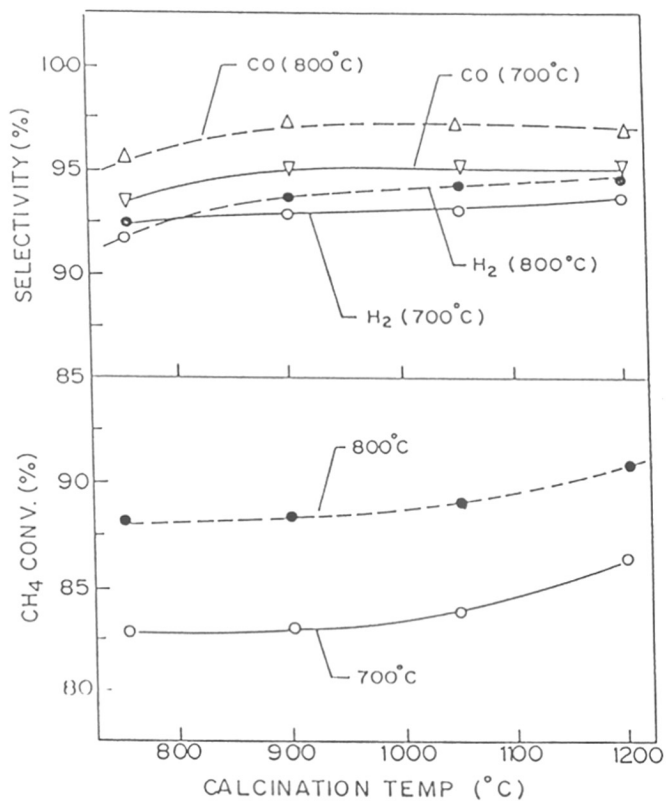


Fig. 3.2.2.:Effect of calcination temperature of the NiO-MgO on its activity and selectivity in the oxidative conversion of methane to syngas at 700°C and 800°C (CH_4/O_2 ratio in the feed = 1.8, GHSV = $5.1 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$)

complete NiO-MgO solid solution with increasing the catalyst calcination temperature. However, a change in the catalyst prereduction (by H₂ for 1h) temperature from 500° to 900°C had a very little or no effect on the methane conversion and also on the selectivity for CO and H₂ in the process (Fig.3.2.3).

e) Effect of CH₄/O₂ feed ratio

Results showing the influence of CH₄/O₂ ratio in the feed on the methane conversion and selectivity for CO and H₂ in the process at 700°C are presented in Fig. 3.2.4. The effect of CH₄/O₂ ratio on the methane conversion is strong ; the conversion is decreased with increasing the CH₄/O₂ ratio, as less amount of O₂ is available for the reaction. However, there is a small increase in the selectivity for both CO and H₂ with increasing the CH₄/O₂ ratio.

d) Influence of GHSV

The influence of gas hourly space velocity (GHSV) of the methane feedstock on the process performance is shown in Fig. 3.2.5. The results indicate that the conversion passes through maximum, the CO selectivity increases with increasing GHSV. The increase in the selectivity of the reaction indicates that it is controlled by kinetics rather than the thermodynamic equilibrium. The production of CO is also much higher (one to three order of magnitude) than that observed previously (1,3).

e) Influence of Reaction Temperature

The results on the oxidative conversion of methane to syngas over the Ni-MgO catalyst with or without reduction by H₂ at 500°C for 1h. are shown in Fig. 3.2.6 The CO selectivity data at the reaction equilibrium (3) are also included in Fig.3.2.6. The high catalytic activity of both NiO/MgO (Fig.3.2.6a) and the reduced catalyst, Ni/MgO (Fig. 3.2.6b) in the oxidation of methane to syngas (mol ratio H₂/CO = 2.0) is evident at different temperatures (300-700°C) with high conversion and CO selectivity. The reaction over NiO/MgO, starts at higher temperatures than that over Ni/MgO. The NiO/MgO catalyst is expected to be reduced by the H₂ formed in the reaction at temperatures ≥ 550°C. It is interesting to note that not only the unreduced catalyst but also the reduced one showed catalytic activity at temperatures below 500°C only after they have been used in the reaction at ≥ 500°C. This suggests that the active sites responsible for the low temperature catalytic activity/selectivity may arise from the further reduction of the catalyst and/or formation of surface carbon species in the following reactions.

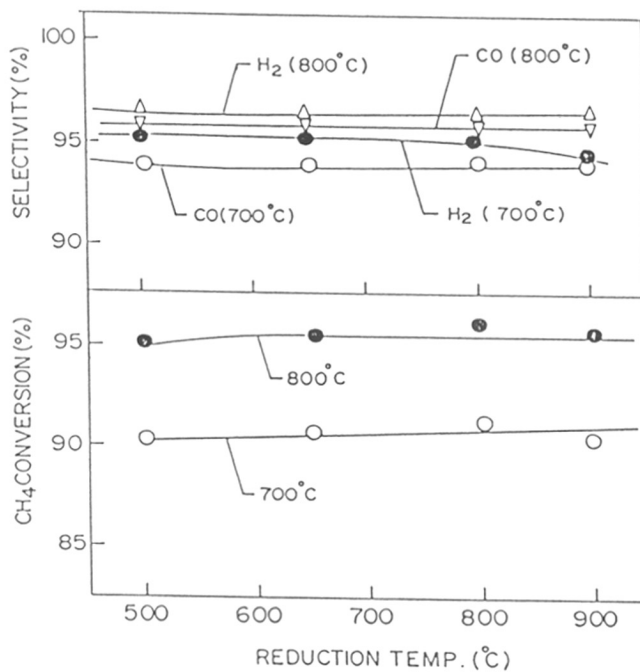


Fig. 3.2.3.: Effect of reduction (by H₂) temperature of the NiO-MgO catalyst on its activity and selectivity in the oxidative conversion of methane to syngas at 700° and 800°C (CH₄/O₂ ratio in the feed = 1.8, GHSV = 5.0 x 10⁵ cm³ g⁻¹ h⁻¹).

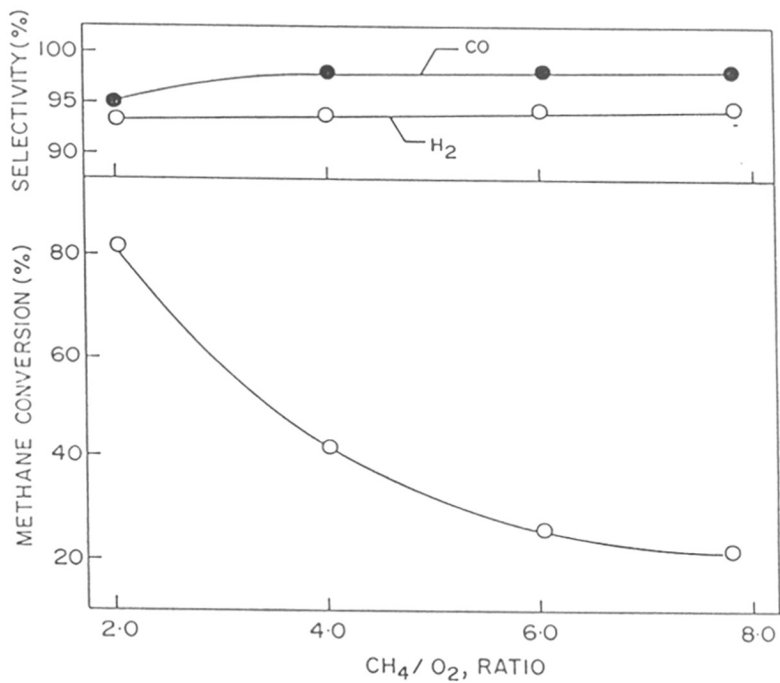


Fig. 3.2.4.: Effect of CH₄/O₂ ratio in the feed on the activity and selectivity of the NiO-MgO catalyst in the oxidative conversion of methane to syngas at 800°C (GHSV= 5.1 x 10⁵ cm³ g⁻¹ h⁻¹).

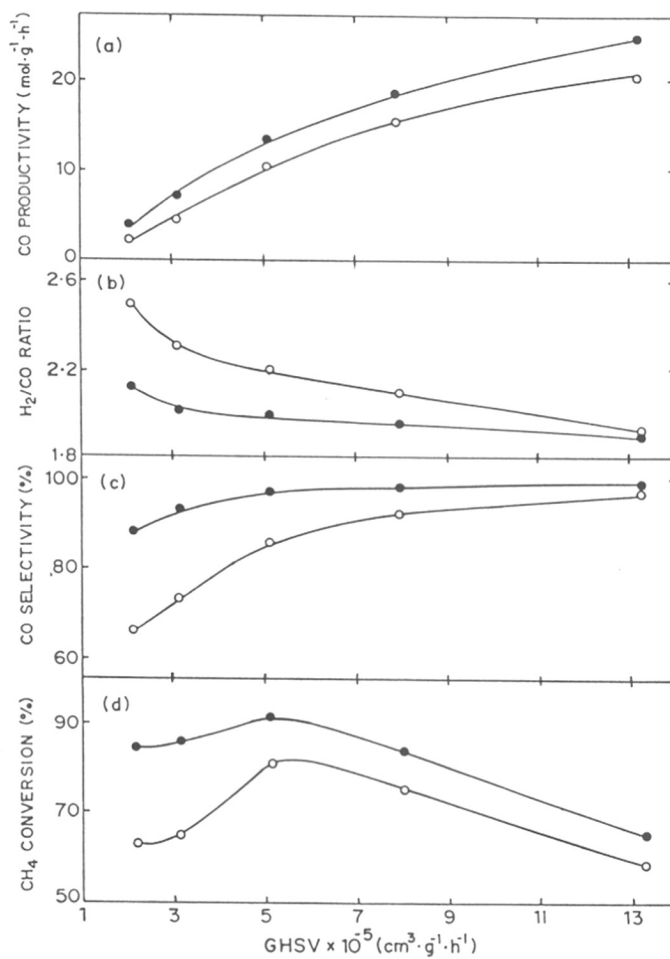


Fig. 3.2.5: Influence of GHSV on catalytic activity/selectivity of Ni/MgO (Ni/Mg ratio = 3.0) at 500°C (O) and 700°C(●)

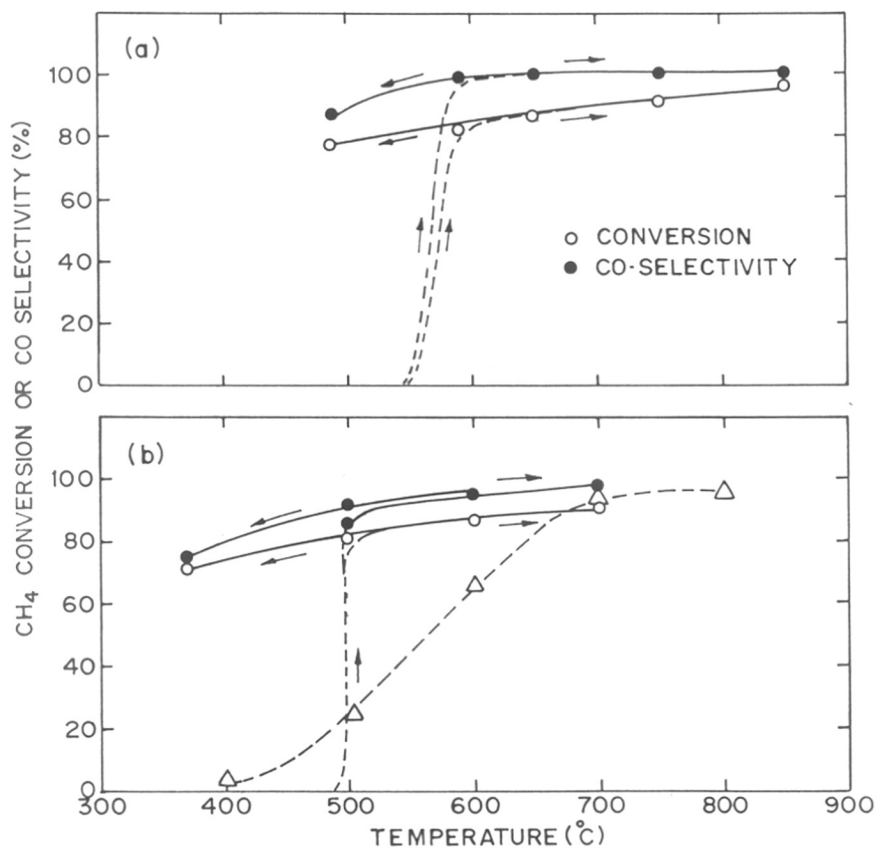


Fig. 3.2.6: Effect on temperature on the catalytic activity/selectivity of the catalysts a) NiO-MgO (unreduced and b) NiO-MgO (reduced). Ni/Mg mol ratio = 3:1, (Feedstock: 67 mol% CH₄, 33 mol% O₂, GHSV = 5.2 x 10⁵ cm³ g⁻¹ h⁻¹; The ordinates correspond to the conversion of CH₄ (O), the selectivity (●), and the CO selectivity under equilibrium conditions (Δ)



The formation of surface carbon was confirmed by O₂ pulse experiment over the used catalysts.

f) Time-on-stream activity / selectivity

Although, the catalyst in the active form is Ni⁰/MgO, the NiO-MgO without prereduction can be used directly for the oxidative conversion of methane to syngas. The NiO from the catalyst is reduced by its reaction with methane,



during the initial short reaction period. Results of the time-on-stream activity/selectivity of the catalyst (without prereduction) in the oxidative methane-to-syngas conversion process at 800°C are presented in Fig. 3 2.7.

The results in (Fig. 3.2.7) show that there is no significant change in the conversion of methane and also in the selectivity for CO and H₂ for a period of at least 14h. The initial period of 30 min. was enough to attain a steady activity/selectivity of the catalyst even though the catalyst was not reduced before starting the reaction.

3.2.2.2 Oxidative Conversion of Methane to Syngas over CoO-MgO Catalysts

The results in Table 3.2.2 reveal the possibility for obtaining synthesis gas with H₂/CO ratio of 1.8-2.0 (which is required for methanol and Fischer-Tropsch synthesis) at high conversion and selectivity from methane by partial oxidation at 700°C and at extremely high space velocity (5.1 x 10⁵ cm³ g⁻¹ h⁻¹) which is over two orders of magnitude greater than that used in the steam reforming of methane, using catalyst with a Co/Mg ratio of 0.5-10.0. The selectivity for CO and H₂ decreased with decreasing reaction temperature. This fact reveals that the formation of CO and H₂ in the reactor at the high space velocities used is kinetically controlled.. Although the catalysts were reduced by hydrogen before the reaction, the catalyst prereduction is not a pre-requisite. However, the unreduced catalysts showed activity in the reaction only at ≥ 600°C; the catalysts are reduced by the H₂ formed in the reaction at ≥ 600°C and then can be used for the reaction at < 600°C. It may be noted that even the prereduced catalyst showed

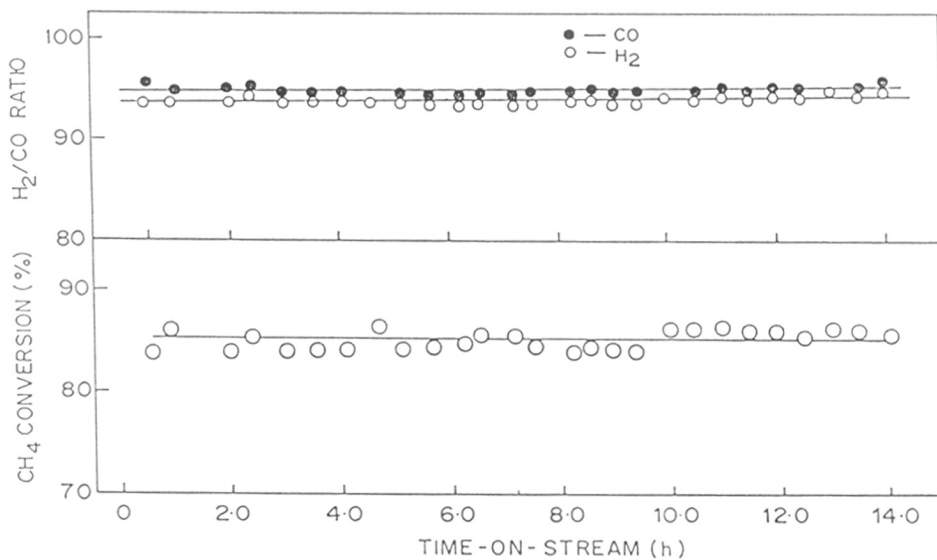


Fig. 3.2.7.: Time-on-stream activity and selectivity of the NiO-MgO catalyst in the oxidative conversion of methane to syngas at 800°C ($\text{CH}_4/\text{O}_2 = 2.0$, GHSV = $5.1 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$)

Table 3.2.2. Activity and selectivity of reduced CoO-MgO catalyst (with different Co/Mg ratios) in oxidative conversion of methane to CO and H₂ at different temperatures (Feed: 67mol% CH₄ and 33 mol% O₂; gas hourly space velocity (GHSV) at STP, 5.1 x 10⁵ cm³ g⁻¹ h⁻¹, pressure 1atm)

Co/Mg ratio	Temp (°C)	CH ₄ conv. (%)	selectivity (%)		H ₂ /CO ratio	STY (mol. g ⁻¹ h ⁻¹)	
			H ₂	CO		H ₂	CO
0.0 (pure MgO)	700	No reaction					
0.1	700	34.9	75.6	79.4	1.90	8.1	4.3
	600	16.0	57.6	73.0	1.58	2.8	1.8
0.5	700	63.7	80.2	88.5	1.81	15.6	8.6
	600	59.5	80.1	87.2	1.84	14.6	8.0
	500	48.8	73.4	80.4	1.83	11.0	6.0
1.0	700	66.4	80.7	91.7	1.76	16.4	9.3
	600	60.1	77.0	88.5	1.74	14.2	8.2
	500	55.9	75.3	86.4	1.74	12.9	7.4
3.0	700	75.1	90.1	91.8	1.96	20.6	10.5
	600	62.3	88.2	90.2	1.96	16.9	8.6
	500	58.1	82.3	87.3	1.89	14.7	7.8
10.0	700	77.2	86.5	93.1	1.86	20.5	11.0
	600	69.9	82.1	91.6	1.69	17.6	9.8
	500	64.8	81.0	86.5	1.86	16.1	8.6
∞ (i.e. CoO)	700	Unsteady reaction (with temperature oscillations) resulting in mostly carbon dioxide and water formation					

activity at $< 600^{\circ}\text{C}$ only after being used in the reaction at $\geq 600^{\circ}\text{C}$. This fact indicates that probably active sites responsible for the catalytic activity/selectivity are created during the reaction at the higher temperature. The reported data were collected following the temperature sequence given in Table 3.2.2.

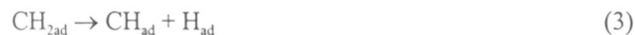
3.2.2.3 Oxidative Conversion of Methane to Syngas over NiO-CoO-MgO Catalyst

The performance of the CoO-MgO (Co : Mg = 1 : 1), NiO-MgO (Ni : Mg = 1 : 1) and NiO-CoO-MgO (Ni : Co : Mg = 0.5 : 0.5 : 1.0) in the oxidative conversion of methane to syngas at a very low contact time (GHSV = $5.1 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$) for different CH_4/O_2 ratios in the feed at 700°C , compared in Fig.3.2.8. The performance of the CoO-MgO catalyst is inferior to that of the two good catalysts. Also, the replacement of half of the NiO from the NiO-MgO catalyst by CoO has a little or no effect on the conversion and selectivity in the process.

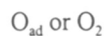
Also, our later studies revealed that the addition of cobalt to NiO-MgO has a beneficial effect, particularly regarding carbon deposition on the surface of the catalyst during methane-to-syngas conversion reactions (Chapter 4.2).

3.2.2.4 Probable Reaction Mechanism

The oxidative methane-to-syngas conversion reaction over the reduced nickel and/or cobalt containing catalyst is expected to proceed through a step-wise homolytic decomposition of methane molecule on the Ni and / or Co sites resulting into adsorbed hydrogen and adsorbed carbon species (CH_x , $x=1-3$) (4,5) simultaneously with the dissociation of O_2 to adsorbed O-atoms (6) as follows,



and



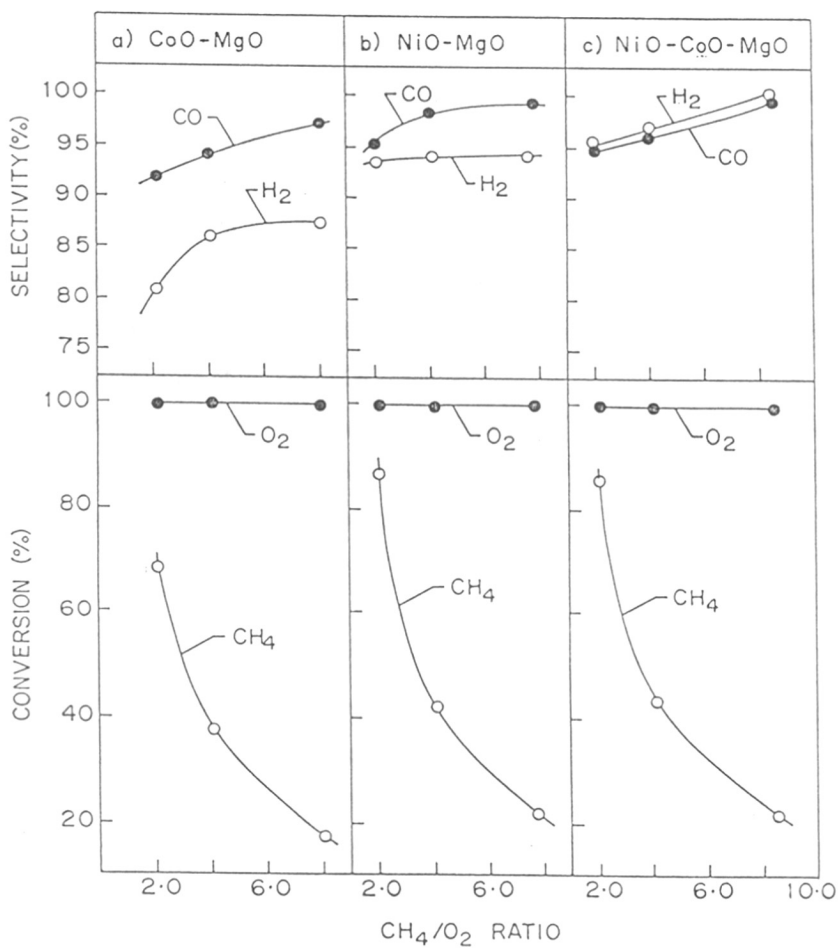


Fig. 3.2.8: Oxidative conversion of methane to CO and H₂ over CoO-MgO, NiO-MgO and NiO-CoO-MgO catalysts at 700°C for different CH₄/O₂ ratios in the feed (GHSV = 5.1 x 10⁵ cm³ g⁻¹ h⁻¹)



Carbon monoxide is formed as a primary product (6). Hydrogen, which is also a primary product, is formed by the combinative desorption of adsorbed H-atoms



3.2.3 CONCLUSIONS

From this investigation, the following important conclusions can be drawn.

- NiO-MgO (Ni/Mg = 1.0-3.0) is a highly promising catalyst for the oxidative conversion of methane to syngas at a very low contact time. It shows high activity and selectivity for both CO and H₂, high stability (or long life) and also very high productivity in the process at a very high space velocity (5.0 x 10⁵ cm³ g⁻¹ h⁻¹).
- The prereduction by H₂ at different temperatures (500-900oC) has only a little effect on the catalytic activity of the NiO-MgO catalyst. The catalyst temperature has also only a small effect on the performance of the NiO-MgO catalyst.
- The performance of the CoO-MgO catalyst is inferior to NiO-CoO-MgO and NiO-MgO catalysts. The replacement of half of the NiO from the NiO-MgO catalysts by CoO has little or no effect on the conversion and selectivity in the process.

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CHAPTER-3.3

OXIDATIVE CONVERSION OF METHANE TO SYNGAS OVER Ru- OR Pt-CONTAINING NiO-MgO SOLID SOLUTIONS

3.3.1 EARLIER LITERATURE AND OBJECTIVES OF THE PRESENT WORK

In the past 8-9 years research activities on the oxidative conversion of methane to syngas using a number of nickel, cobalt, and noble metal containing catalysts caught a tremendous momentum (1,2). In the earlier studies of our group, a number of Ni or Co containing catalysts such as NiO-MgO (3), NiO-CaO (4), NiO-Yb₂O₃ (5), NiO-rare earth oxides (6), CoO-MgO (7), CoO-rare earth oxides (8) Ni/Al₂O₃ (9), CoO.NiO-Yb₂O₃ or ThO₂, and ZrO₂ (10) NiO-ThO₂ or ZrO₂ or UO₃ (11), showed, high activity and selectivity in this process at a very low contact time ($5.1 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$). However, among the nickel containing catalysts, the NiO-MgO, which is a solid solution, showed the best performance. Earlier studies on NiO-Al₂O₃ catalyst (12) revealed that the addition of noble metal (Pt and Ru) to the catalyst has a beneficial effect on its performance in this process. It is also therefore, interesting to study this process over noble metal containing NiO-MgO solid solution for developing a still better catalyst for this process. The present investigation was undertaken for this purpose.

3.3.2 RESULTS AND DISCUSSION

3.3.2.1 Temperature Programmed Reduction (TPR)

The TPR of the NiO-MgO, Ru/NiO-MgO and Pt/NiO-MgO catalysts was carried out in a flow of H₂ / Ar mixture (2.0 mol% H₂) from 50° to 900°C at a linear heating rate of 10°C min.⁻¹ and further at 900°C for 1h. Results of the TPR of these catalysts are presented in Fig.3.3.1. The amount of H₂ consumed in the TPR run and the degree of reduction of NiO from these catalysts are given in Table 3.3.1.

The TPR results show that the peak maximum temperature in the TPR of all the catalysts is 900°C, which is the maximum temperature of the TPR. The TPR curves are quite similar to that observed for a typical NiO-MgO complete solid solution (13, 14). The degree of reduction

of NiO from the NiO-MgO catalyst in the TPR is small (11.5%). The degree of reduction is, however, increased appreciably because of the presence of Ru or Pt in the catalyst (Table 3.3.2).

Table 3.3.1 Data on the degree of reduction of NiO in the NiO-MgO, Pt/NiO-MgO and Ru/NiO-MgO catalysts.

Catalyst	H ₂ consumed (mmol. g ⁻¹)	Degree of NiO reduction (%)
Pt/NiO-MgO	2.81	24.7
Ru/NiO-MgO	2.98	26.3

For all the catalysts, there is a hump on the TPR curves in the temperature range of 400°-600°C. The hump is, however, shifted towards the lower temperature side because of the presence of the noble metal, particularly Ru, in the catalyst. A small TPR peak at about 170°C is observed for the Ru/NiO-MgO catalyst. This peak is due to the reduction of ruthenium oxide to Ru at the low temperature.

The increase in the degree of reduction of NiO due to the presence of Pt or Ru in the catalyst is mostly because of the dissociative adsorption of hydrogen on the noble metal followed by a spillover of atomic hydrogen. This spillover hydrogen (hydrogen atom) which are very active, are responsible for the reduction of more NiO from the NiO-MgO solid solution. The highly active spillover hydrogen is also for the observed shift of hump on the TPR curve (at 400°-600°C) to lower temperature.

3.3.2.2 Oxidative Methane-to-Syngas Conversion

The NiO-MgO catalyst with or without containing Ru or Pt are compared for their performance in the oxidative conversion of methane to syngas in Table 3.3.2. The observed high activity and selectivity of the catalyst due to the presence of Pt or Ru is attributed to the increased reduction of NiO from the NiO-MgO solid solution due to the spillover of hydrogen from the noble metal. These results are consistent with those observed for the NiO/Al₂O₃ catalyst with or without containing Pt, Pd or Ru (12).

Results showing the influence of temperature on the methane conversion and selectivity for the H₂ and CO in the catalytic process over the Ru/NiO-MgO and Pt/NiO-MgO catalysts,

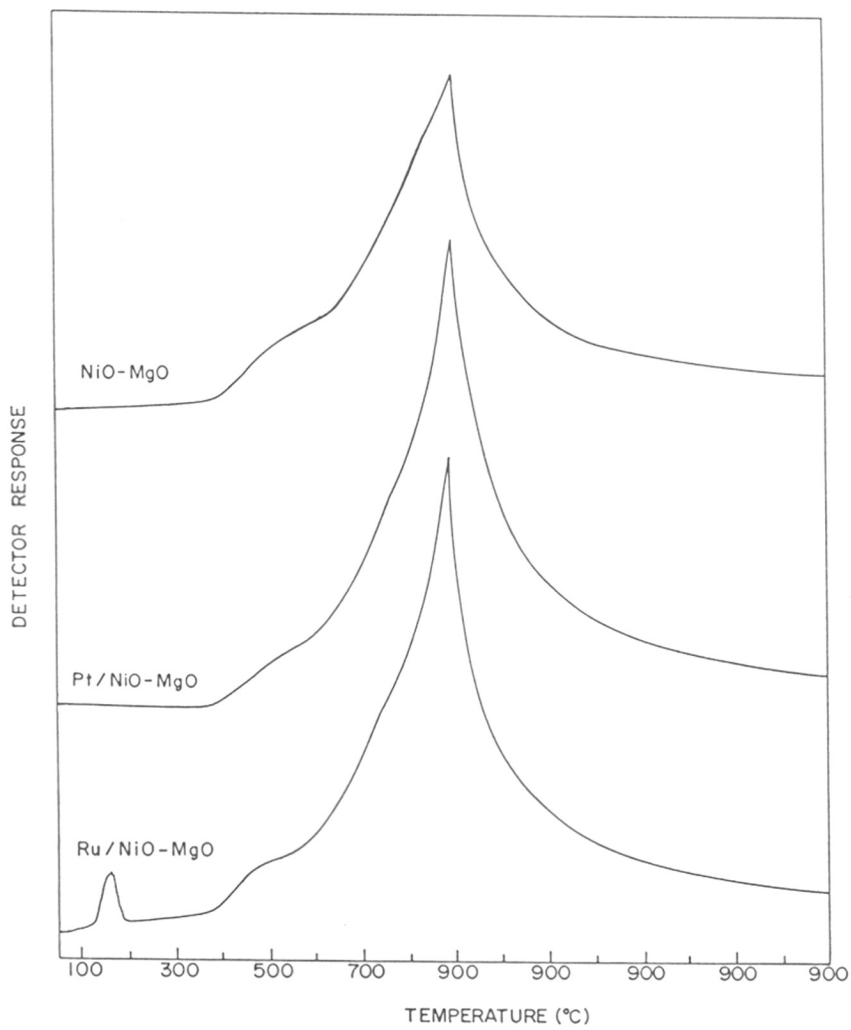


Fig.3.3.1:TPR of NiO-MgO with or without containing Pt or Ru

with or without prereduction by H_2 at $500^\circ C$ for 1h, are presented in Figs.3.3.2 and 3.3.3. For both the noble metal containing NiO-MgO catalysts, the prereduction before use has a beneficial

Table:3.3.2 Comparison of Ru-and Pt/NiO-MgO catalysts with NiO-MgO for the oxidative conversion of methane to syngas at $800^\circ C$

Catalyst	CH ₄ conversion (%)	Selectivity (%)	
		H ₂	CO
<u>A) Catalysts reduced (before reaction) at $500^\circ C$ by H_2</u>			
NiO-MgO	87.6	96.3	96.1
Pt/NiO-MgO	96.5	98.7	96.5
Ru/NiO-MgO	95.0	98.0	97.2
<u>B) Catalyst without reduction</u>			
NiO-MgO	86.2	93.4	94.6
Pt/NiO-MgO	87.0	92.0	96.0
Ru/NiO-MgO	94.0	95.0	95.5

effect on the catalyst performance; both the methane conversion activity and selectivity for CO and H_2 of the catalyst in the process are increased due to the catalyst prereduction by H_2 . The reduction of NiO from NiO-MgO at $500^\circ C$ is very low (Fig. 3.3.1). However, 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.



The reduction of NiO during the initial reaction is expected to increase in the presence of Pt or Ru because of the spillover of hydrogen formed in the homolytic decomposition of methane on the noble metals.

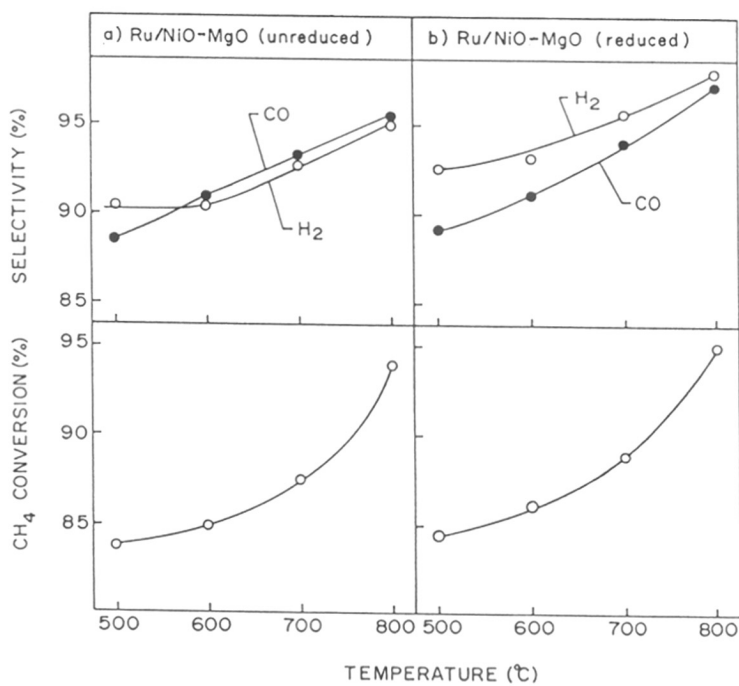


Fig.3.3.2:Temperature dependence of the activity and selectivity of Ru/NiO-MgO with or without its prereduction in the oxidative conversion of methane to CO and H₂.

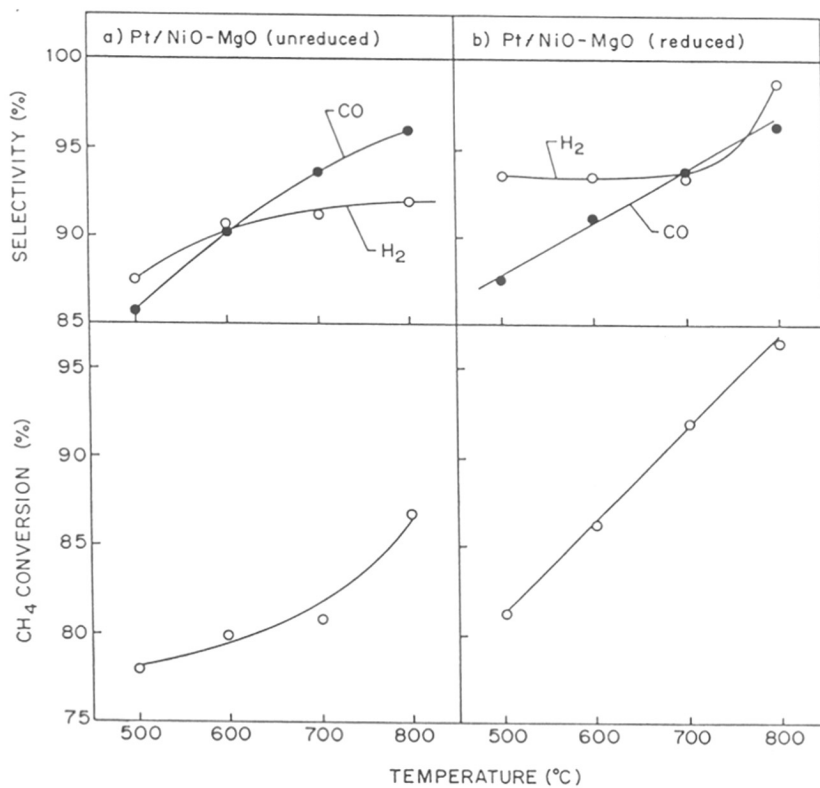


Fig.3.3.3: Temperature dependence of the activity and selectivity of Pt/NiO-MgO with or without its prereduction in the oxidative conversion of methane to CO and H₂.

The catalytic oxidative methane-to-syngas conversion reaction is expected to proceed through a step-wise homolytic decomposition of methane molecule on the Ni and Pt or Ru sites resulting into adsorbed hydrogen, adsorbed carbon and partially hydrogenated carbon species (CH_x , where $x = 1-3$) [15,16] simultaneously with the dissociation of O_2 to adsorbed O-atoms [17] as follows,



and



Thus, the carbon monoxide, hydrogen and CO_2 are formed as the primary products.

The observed high conversion and selectivity of the noble metal containing catalysts indicates that reactions 2-4 are more favored in the presence of Pt or Ru in the catalyst.

3.3.3 CONCLUSIONS

Following important conclusions can be drawn from the TPR and the oxidative methane-to-syngas conversion over the NiO-MgO solid solution with or without containing Pt (1.0 wt%) or Ru (1.0 wt%).

- The amount of hydrogen consumed and consequently the degree of reduction of NiO from the NiO-MgO catalyst are increased because of the addition of Pt or Ru to the catalyst. The increase in the degree of reduction of the catalyst is attributed mainly to the spillover of hydrogen (highly active atomic hydrogen) on the noble metal.
- Both the catalytic activity and selectivity (in the oxidative methane-to-syngas process) of the NiO-MgO solid solution are increased appreciably because of the addition of the Pt or Ru to the solid solution.

- The prereduction by the hydrogen (at 500°C) of the Pt or Ru/NiO-MgO catalysts is beneficial for the oxidative conversion of methane to syngas; both the conversion and selectivity are increased due to the prereduction.

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CHAPTER-3.4

OXIDATIVE CONVERSION OF METHANE TO CO AND H₂ OVER Pt OR Pd CONTAINING ALKALINE AND RARE EARTH OXIDE CATALYSTS

3.4.1 Earlier Literature and Objectives of the Present Work

A very significant progress in the oxidative conversion of methane to syngas with high conversion and selectivity particularly at very low contact time (about 1 ms), using nickel [1-6], cobalt [6-8] or noble metal [9-19] containing catalysts, has been made. The oxidative methane-to-syngas conversion over noble metal catalysts at higher contact times has also been reported [11,14-16 20-23]. The earlier results on the oxidative conversion of methane to syngas over noble metal catalysts at both the low and high contact times are summarized in Table-3.4.1.

Our earlier studies in our group indicated that Ni and/or Co/MgO [5-7], Ni/CaO [1], Ni/Yb₂O₃ [2] and Ni or Co/rare earth oxide [3,8] catalysts show high methane conversion activity (above 90%) and high selectivity (above 90%) for both CO and H₂ in the partial oxidation of methane to syngas at very low contact time (≈ 1 ms). It is, also, interesting to study the activity and selectivity of Pt and Pd containing MgO, CaO and rare earth oxide catalysts in the process at the low contact time. In most of the earlier studies on the oxidative conversion of methane over Pt and Pd catalysts, either the support used for the noble metal is different from alkaline and rare earth oxide [9-15, 19-21] and/or the reaction contact time is higher [11,14-17,19,20,22].

The present investigation was undertaken for studying the activity and selectivity of Pd and Pt containing MgO, CaO and rare earth oxide (viz. La₂O₃, Pr₆O₁₁, Nd₂O₃, Sm₂O₃, Gd₂O₃, Dy₂O₃ and Er₂O₃) catalysts in the oxidative methane-to-syngas conversion process at very low contact time [space velocity : $5.0 (\pm 0.2) \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$]

Because of the low contact time for the reaction, the productivity (or space-time-yield) of syngas in the process is very high, making it possible to use a very small volume reactor and thereby reducing drastically both the catalyst cost and the capital cost for the reactor.

Table-3.4.1 Results of earlier studies on oxidative conversion of methane to CO and H₂ over supported noble metal catalysts

Catalyst	Reaction conditions			CH ₄ Conversion (%)	Selectivity (%)		Ref.
	Temp. (°C)	CH ₄ /O ₂ ratio	Space velocity (h ⁻¹)		CO	H ₂	
3.5wt% Pd /La ₂ O ₃	1200	2.0	1.0 x 10 ⁵	56.0	83.0	57.0	11
0.5wt% Pd / monolith	1270	2.0	1.0 x 10 ⁵	52.0	72.0	53.0	11
1wt% Pd/La ₂ O ₃	750	8.0	5.0 x 10 ³	49.3	99.5	—	16
1.0 wt% Pd / CeO ₂	750	8.0	5.0 x 10 ³	35.0	99.4	—	16
1.0 wt% Pd/Al ₂ O ₃	777	2.0	4.0 x 10 ⁴	93.0	96.0	98.0	15
2.5 wt% Pd/Al ₂ O ₃	800	2.0	5.1 x 10 ^{5*}	46.5	92.0	60.2	14
2.5wt% Pd-Ni/Al ₂ O ₃	800	2.0	5.1 x 10 ^{5*}	70.3	93.4	86.6	13
Pd/ZrO ₂	600	8.0	-----	24.0	90.0	90.0	20
0.5 wt% Rh/Sm ₂ O ₃	700	2.0	1.0 x 10 ⁶	80.0	90.0	----	19
Rh/SiO ₂	700	2.0	1.2 x 10 ⁴	1.0	96.0	93.0	21
RhVO ₄ /SiO ₂	700	2.0	1.2 x 10 ⁴	10.0	91.0	91.0	21
1.0 wt%Ru/Al ₂ O ₃	777	2.0	4.0 x 10 ⁴	94.0	97.0	99.0	15
2.5wt% Ru/Al ₂ O ₃	800	2.0	5.0 x 10 ⁴	74.0	95.1	95.0	13
0.5wt% Ru/Al ₂ O ₃	700	2.0	3.5 x 10 ⁶	43.0	70.0	—	28

Table-3.4.1 continued.....

Catalyst	Reaction conditions			CH ₄ Conversion (%)	Selectivity (%)		Ref.
	Temp (°C)	CH ₄ /O ₂ ratio	Space velocity (h ⁻¹)		CO	H ₂	
Yb ₂ Ru ₂ O ₇	777	2.0	4.0 x 10 ⁴	83.0	91.0	95.0	22
Pr ₂ Ru ₂ O ₇	777	2.0	4.0 x 10 ⁴	89.0	94.0	98.0	14
0.1 wt% Ru/Al ₂ O ₃	777	2.0	4.0 x 10 ⁴	61.0	78.0	83.0	14
4.7 wt% Pt/monolith	1130	2.0	1.0 x 10 ⁵	67.0	94.0	78.0	11
4.0 wt% Pt/ Al ₂ O ₃	900 - 1100	1.8	1.0 x 10 ⁶	80.0	95.0	75.0	12
10 wt% Pt / Al ₂ O ₃	850- 1150	1.8	1.0 x 10 ⁶	100.0	90.0	90.0	9
Pt/Al ₂ O ₃ monoliths	800 - 1200	1.8	1.0 x 10 ⁵ - 1.0 x 10 ⁶	85.0	93.0	82.5	17
0.5 wt% Pt/ Al ₂ O ₃	800	2.0	4.0 x 10 ³	51.0	73.0	65.0	23
1.0 wt% Pt/Al ₂ O ₃	777	2.0	4.0 x 10 ⁴	95.0	96.0	99.0	15
2.5 wt% Pt- Ni/Al ₂ O ₃	800	2.0	5.0 x 10 ^{5*}	88.1	96.5	97.5	13
La ₂ MgPO ₆	777	2.0	4.0 x 10 ⁴	80.0	89.0	93.0	15

*cm³g.⁻¹h.⁻¹

3.4.2 RESULTS AND DISCUSSION

3.4.2.1 Catalyst Characterization

Data for the surface area and hydrogen chemisorption (which is measure of the dispersion or surface area of noble metal) at 40°C on the Pt and Pd containing catalysts are given in Table-3.4.2. The concentration of noble metal in all the catalysts is the same (1.0 wt%). A comparison of the data (Table3.4.2) shows that the catalysts differ widely from each other in their specific surface area and also in their H₂ chemisorption. The highest surface area is shown by the Pt and Pd catalysts containing MgO and the lowest by the catalysts containing Pr₆O₁₁. However, the Pt and Pd catalysts containing CaO show the lowest hydrogen chemisorption and ones containing Pr₆O₁₁ show highest H₂ chemisorption.

3.4.2.2 Activity / Selectivity of Pt Catalysts

The results showing the influence of alkaline and rare earth oxides on the activity/selectivity of Pt containing catalysts in the oxidative conversion of methane to syngas at very low contact time [GHSV= 5.0 (± 0.2) x 10⁵ cm³ g⁻¹ h⁻¹] at 700° and 800°C are presented in Table-3.4.3. The activity of Pt/La₂O₃ catalyst could not be measured because of the temperature oscillations in the catalytic process at 700°C and 800°C.

A comparison of Pt containing catalysts (Table-3.4.1) for their catalytic activity/selectivity and CO productivity shows that the Pt/Gd₂O₃ and Pt/MgO are most active and selective catalysts and the Pt/Nd₂O₃ is the least active catalyst for the oxidative conversion of methane to syngas. It may be noted that there is no direct correlation between the catalytic activity/selectivity and the H₂ chemisorption on the catalyst. This indicates that the catalytic activity does not depend directly on the dispersion of Pt but also on the other substrate (i.e. alkaline and rare earth oxides).

Earlier results on the oxidative conversion of methane to syngas for Pt/Al₂O₃ catalysts [9,11-13,17-23] are given in Table-3.4.1. Since reaction conditions are somewhat different from that used in the present case, a direct comparison of the catalytic activity/selectivity of the catalysts (Table-3.4.3) with earlier ones is difficult. Nevertheless, the Pt/MgO and Pt/Gd₂O₃ catalysts show good performance in the process at 700°-800°C and at the high space velocity.

Table 3.4.2 Surface area and H₂ chemisorption (at 40°C) data for the Pt and Pd containing alkaline and rare earth oxide catalysts

Catalyst	Surface Area (m ² .g ⁻¹)	H ₂ chemisorbed (μ mol.g ⁻¹)
	22.3	4.1
Pt/CaO	5.1	<0.5
Pt/La ₂ O ₃	7.3	1.6
Pt/Pr ₆ O ₁₁	1.1	4.7
Pt/Nd ₂ O ₃	1.9	0.6
Pt/Sm ₂ O ₃	4.8	0.3
Pt/Gd ₂ O ₃	3.2	1.3
Pt/Dy ₂ O ₃	3.8	3.1
Pt/Er ₂ O ₃	3.1	0.4
Pd/MgO	19.9	4.7
Pd/CaO	4.4	<0.5
Pd/La ₂ O ₃	7.5	3.0
Pd/Pr ₆ O ₁₁	2.4	6.1
Pd/Nd ₂ O ₃	3.4	1.4
Pd/Sm ₂ O ₃	5.4	2.7
Pd/Gd ₂ O ₃	3.0	1.5
Pd/Dy ₂ O ₃	3.8	2.6
Pd/Er ₂ O ₃	3.2	1.3

3.4.2.3 Activity/Selectivity of Pd Catalysts

The Pd containing alkaline and rare earth oxide catalysts are compared for their performance in the oxidative conversion of methane to syngas at 700° and 800°C [GHSV= 5.0 (± 0.2) $\times 10^5$ cm³ g⁻¹ h⁻¹] in Table-3.4.4.

It is interesting to know that unlike the Pt/MgO and Pt/CaO catalysts, the Pd/MgO, Pd/CaO catalysts show a comparable performance. However, among the Pd catalysts, the Pd/Sm₂O₃ shows the best performance. The Pd/Gd₂O₃ catalyst also shows a good performance but at the higher temperature (at 800°C). In general, the Pd catalysts (Table-3.4.4) show lower selectivity for both H₂ and CO as compared to the Pt catalysts (Table-3.4.3).

Earlier results on the oxidative conversion of methane to syngas over supported Pd catalysts [11,13-16,20] are presented in Table-3.4.1. The H₂ and CO selectivities obtained for the earlier Pd catalysts are also low. It may be noted that the high CO selectivity observed earlier over Pd/La₂O₃ and Pd/CeO₂ [16] is not essentially due to catalytic reaction but may be due to non-catalytic gas-solid reaction [as per the reaction stoichiometry : CH₄ + 0.5O₂ → CO + 2H₂, the methane conversion of 49.3% or 35% cannot be obtained for the CH₄/O₂ ratio (in the feed) of 8.0. For the Pd catalysts also, there is no direct relationship between the catalyst activity/selectivity and the H₂ chemisorption (or dispersion of Pd). Thus, apart for the noble metal, the alkaline and rare earth oxide also plays an important role in deciding the activity/selectivity of both the Pt and the Pd catalysts as follows.

3.4.2.4 Influence of support

The oxidative methane-to-syngas conversion reaction over the noble metal catalyst is expected to proceed through a step-wise homolytic decomposition of methane molecule on the Pt or Pd sites resulting into adsorbed hydrogen, adsorbed carbon and partially hydrogenated carbon species (CH_x, where x =1-3) [24,25] simultaneously with the dissociation of O₂ to adsorbed O-atoms [26] as follows,



Table 3.4.3 Results of oxidative conversion of methane to CO and H₂ over Pt (1wt%) containing alkaline and rare earth oxide catalysts

Catalyst	CH ₄ conversion (%)	Selectivity (%)			H ₂ /CO ratio	CO productivity (mol.g ⁻¹ .h ⁻¹)
		H ₂	CO	CO ₂		
<u>Temperature:700°C</u>						
Pt/MgO	69.1	83.2	90.3	9.7	1.8	9.3
Pt/CaO	54.7	66.4	77.7	22.3	1.7	6.4
Pt/La ₂ O ₃	temperature oscillations were observed					
Pt/Pr ₆ O ₁₁	49.8	49.5	74.6	25.4	1.3	5.7
Pt/Nd ₂ O ₃	47.3	64.9	82.4	17.6	1.6	5.9
Pt/Sm ₂ O ₃	58.9	76.1	89.8	10.2	1.7	7.6
Pt/Gd ₂ O ₃	70.2	82.6	91.6	8.4	1.8	9.5
Pt/Dy ₂ O ₃	58.8	74.5	92.5	7.5	1.6	8.1
Pt/Er ₂ O ₃	58.5	65.5	90.8	9.2	1.4	8.2
<u>Temperature:800°C</u>						
Pt/MgO	73.4	84.9	92.5	7.5	1.8	10.2
Pt/CaO	57.3	75.2	82.9	17.1	1.8	7.2
Pt/La ₂ O ₃	temperature oscillations were observed					
Pt/Pr ₆ O ₁₁	55.1	68.7	80.5	19.5	1.7	6.9
Pt/Nd ₂ O ₃	45.6	61.3	84.2	15.8	1.4	5.8
Pt/Sm ₂ O ₃	62.4	76.4	90.0	10.0	1.7	8.5
Pt/Gd ₂ O ₃	72.7	83.5	94.2	5.8	1.8	11.1
Pt/Dy ₂ O ₃	64.7	81.2	94.2	5.8	1.7	9.2
Pt/Er ₂ O ₃	61.1	72.5	93.3	6.7	1.5	8.7

Table 3.4.4. Results of oxidative conversion of methane to CO and H₂ over Pd (1wt%) containing alkaline and rare earth oxide catalyst

Catalyst	CH ₄ conversion (%)	Selectivity (%)			H ₂ /CO ratio	CO productivity (mol.g ⁻¹ .h ⁻¹)
		H ₂	CO	CO ₂		
<u>Temperature:700°C</u>						
Pd/MgO	53.9	75.2	80.9	19.1	1.8	6.5
Pd/CaO	50.1	61.0	80.1	19.9	1.5	5.9
Pd/La ₂ O ₃	45.7	46.7	89.4	10.7	1.0	6.2
Pd/Pr ₆ O ₁₁	41.3	52.7	68.9	31.1	1.5	4.3
Pd/Nd ₂ O ₃	48.6	59.7	83.1	16.9	1.4	6.3
Pd/Sm ₂ O ₃	58.0	78.9	89.5	10.5	1.8	7.9
Pd/Gd ₂ O ₃	52.3	73.2	87.0	13.0	1.7	7.1
Pd/Dy ₂ O ₃	53.9	65.5	86.6	13.4	1.5	7.7
Pd/Er ₂ O ₃	47.5	61.4	84.4	15.6	1.4	6.4
<u>Temperature:800°C</u>						
Pd/MgO	58.1	73.1	87.2	12.8	1.7	7.6
Pd/CaO	59.7	86.1	76.5	23.5	12.2	8.0
Pd/La ₂ O ₃	44.7	44.7	88.6	11.4	1.0	6.0
Pd/Pr ₆ O ₁₁	48.1	73.2	73.9	26.1	2.0	5.3
Pd/Nd ₂ O ₃	55.8	71.5	90.1	9.9	1.6	7.9
Pd/Sm ₂ O ₃	65.4	79.8	89.6	10.4	1.8	8.9
Pd/Gd ₂ O ₃	60.9	77.2	90.5	9.5	1.7	8.5
Pd/Dy ₂ O ₃	53.9	65.5	86.6	13.4	1.5	7.7
Pd/Er ₂ O ₃	51.1	63.4	87.1	12.9	1.4	7.2



and



Carbon monoxide and CO_2 are formed as a primary products (27) . Hydrogen, which is also a primary product, is formed by the combinative desorption of adsorbed H- atoms. The observed decrease in the carbon / coke deposition due to the cobalt addition also seems to result mostly from the complete combustion of the coke precursors, such as adsorbed partially hydrogenated carbon species. Earlier studies (26) showed that adsorbed methyl radicals are less reactive (as compared to adsorbed carbon) and lead to the formation of amorphous carbon.

In the present case, since the supported (alkaline and rare earth oxides) used for Pt and Pd are basic in nature, the CO_2 formed in the process is adsorbed strongly (or chemisorbed) on the basic supports. The adsorbed CO_2 is expected to undergo reaction with H-atoms spilled over from the noble metal, as follows.



Reaction-6 is a reverse water gas shift reaction and it is responsible for the observed lower selectivity for H_2 than that of CO (Tables-3.4.3 and 3.4.4). The spillover of H atoms from the noble metals and the chemisorption of CO_2 depends on the basicity and other characteristics (e.g. interaction with noble metal) of the alkaline earth and rare earth oxides. Methane is also adsorbed on the basic metal oxides forming methyl radicals (28-30). Moreover, there is a possibility of a spillover of partially dissociated methane species (CH_x) from noble metal to the basic sites of the support. This seems to be the reason for not getting a direct relationship between the activity/selectivity and the H_2 chemisorption (or noble metal surface area or dispersion) for the Pt- and Pd- catalysts.

3.4.3 CONCLUSIONS

The Pt/ Gd_2O_3 , Pt/MgO and Pd/ Sm_2O_3 catalysts show activity and high selectivity and also high productivity for CO but low selectivity for H_2 , due to the reverse water gas shift

reaction, in the oxidative conversion of methane to CO and H₂ at very low contact time. In general, the activity/selectivity of Pt containing alkaline and rare earth oxide catalysts is higher than the Pd containing catalysts. There is, however, no direct correlation between the H₂ chemisorption (or dispersion of the noble metals) on the Pt or Pd catalysts and their activity/selectivity in the process. The alkaline earth and rare earth oxides are basic in nature and therefore act not only as support for dispersing the noble metals but also play significant role in deciding the activity and selectivity of the Pt or Pd containing alkaline earth and rare earth oxide catalysts in the catalytic process.

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CHAPTER-3.5

PARTIAL OXIDATION OF METHANE TO CO AND H₂ OVER COBALT CONTAINING ZrO₂, ThO₂, UO₂, TiO₂ AND SiO₂ CATALYSTS

3.5.1 EARLIER LITERATURE AND OBJECTIVES OF THE PRESENT WORK

Extensive studies have been made on the oxidative conversion of methane to syngas using a number of Ni or Co containing catalysts, such as NiO-MgO (1), NiO-CaO (2), NiO-rare earth oxides (3,4), NiO-Al₂O₃ (5,6), Ni/Ca_{1-x}Sr_xTiO₃ (7), CoO-MgO (8), CoO-rare earth oxides (9), NiO-CoO-Yb₂O₃ (10), and also using various noble metal catalyst (11-22). The NiO and /or CoO containing MgO, CaO, rare earth oxides or alumina catalysts (1-5, 8-10) showed high catalytic activity in the process at a very low contact time (about 1ms). The noble metal catalysts (11-15) also showed high catalytic activity in the process at a millisecond contact time but these catalyst are very costly as compared to nickel and/or cobalt containing catalysts. Hence for developing a better catalyst for the process, it is also interesting to study the performance of nickel and cobalt catalysts containing other commonly used metal oxide supports, such as ZrO₂, ThO₂, UO₂, TiO₂, and SiO₂ in the oxidative methane -to-syngas conversion process. This investigation was undertaken for this purpose.

3.5.2 Results and Discussion

The data on the surface area of different catalysts are given in Table-3.5.1. A comparison of the surface area of the different NiO, CoO and NiO-CoO containing catalysts shows that in general the surface area of the NiO containing catalyst is highest and that of Co containing catalysts is the lowest. Whereas, the surface area of the NiO-CoO containing catalyst has intermediate value. This shows that because of the addition of cobalt to a nickel containing catalyst, the surface area of the catalyst is decreased markedly.

Results of oxidative conversion of methane over the different Ni, Co, and Ni-Co containing catalysts (reduced at 500°C by H₂) are presented in Table-3.5.1. The results over the unreduced NiO and CoO containing catalysts are given in Table-3.5.2. Following important observations can be made from the results.

Among the Ni containing catalysts, the highest activity and selectivity in the catalytic process are shown by the NiO-ThO₂ catalyst. The NiO-TiO₂ catalyst (reduced at 500°C) shows no activity in the process. However, the NiO-TiO₂ catalyst acquires very significant activity when it is reduced at 800°C. The crystalline phases present in the NiO-TiO₂ catalysts are as follows:

- Unreduced catalyst : NiTiO₃ (major) and NiO (minor)
- Catalyst reduced at 500°C : Ni⁰ (traces), NiO (minor) and NiTiO₃ (major)
- Catalysts reduced at 800°C : Ni⁰ (major) and TiO₂ (major)

Thus, because of the presence of NiTiO₃ (which is difficult to reduce), the catalyst reduced at 500°C does not show any activity in the process. The binary metal oxide phase is formed due to solid-solid reaction between NiO and TiO₂ during the high temperature (900°C) calcination of the catalyst precursors. In all the other reduced catalysts, the major crystalline phases observed are Ni⁰ or Co⁰ (major), NiO or CoO (minor or traces) and corresponding other metal oxide phases (major).

The CoO-ThO₂ and CoO-UO₂ catalysts show poor activity and selectivity in the process as compared to the corresponding nickel containing catalyst. The NiO-CoO-ZrO₂, NiO-CoO-ThO₂ and NiO-CoO-UO₂ catalysts also show lower activity and selectivity as compared to the corresponding catalyst containing nickel alone. However, the rate of carbon deposition on the NiO-CoO containing catalysts is much lower than that for the catalyst containing nickel alone. These results clearly show a beneficial effect of the addition of cobalt in the nickel containing catalysts for reducing drastically the carbon deposition on them in the catalytic process. A similar beneficial effect of the addition of cobalt to NiO-Yb₂O₃ catalyst has also been observed earlier (10).

It may be noted that the prerduction of the catalysts before the reaction is not a must. The performance of the reduced and unreduced NiO and/or CoO containing catalysts (Tables-3.5.1 and 3.5.2) is comparable. The NiO or CoO from the unreduced catalysts is expected to be reduced during the initial catalytic process (1,2). In spite of the carbon deposition on the Ni and Ni-Co containing ZrO₂, ThO₂ and UO₂ catalysts, the activity and selectivity of these catalysts are not affected significantly when they are on the stream at least for 4h. However, the NiO-SiO₂

Table 3.5.1: Results of the conversion of methane to syngas over Ni-containing mixed metal oxide catalysts reduced at 500°C (reaction conditions : feed = 66 mol% CH₄ and 34 mol% O₂, GHSV = 5.2 x 10⁵ cm³.g⁻¹.h⁻¹ and temp. = 700°C)

Catalyst	surface area (m ² g ⁻¹)	CH ₄ conversion (%)	selectivity (%)		H ₂ /CO ratio	carbon deposition x 10 ³ (g .g ⁻¹ .h ⁻¹)
			CO	H ₂		
NiO-ZrO ₂	4.3	76.5	93.8	92.8	1.98	13.1
NiO-CoO-ZrO ₂	2.1	70.1	90.7	91.6	2.02	0.8
NiO-ThO ₂	6.0	90.3	95.2	95.6	2.01	2.3
CoO-ThO ₂	0.6	66.2	89.7	79.7	1.78	---
NiO-CoO-ThO ₂	1.4	80.6	93.0	90.1	1.93	0.1
NiO-UO ₂	2.0	78.7	95.2	92.4	1.94	0.2
CoO-UO ₂	0.5	49.8	81.3	64.2	1.58	---
NiO-CoO-UO ₂	0.8	58.6	90.6	86.6	1.58	0.03
NiO-SiO ₂	67.0	53.6	84.4	73.5	1.74	---
NiO-TiO ₂	4.1	0.0	---	---	---	---
NiO-TiO ₂ ^a	---	52.5	90.3	77.3	1.84	---

^a Reduced at 800°C

Table 3.5.2: Results of the oxidative conversion of methane to syngas over unreduced Ni or Co containing mixed metal oxide catalysts (reaction conditions : feed=66 mol% CH₄ and 34 mol% O₂, GHSV= 5.2 x 10⁵ cm.³ g.⁻¹ h.⁻¹)

catalyst	Reaction temperature (°C)	CH ₄ conversion (%)	Selectivity (%)		H ₂ /CO ratio
			H ₂	CO	
NiO-ThO ₂	800	94.2	96.8	97.1	1.99
	700	90.0	94.8	95.1	1.99
NiO-UO ₂	800	79.4	88.8	95.5	1.86
	700	71.2	82.2	93.4	1.76
CoO-ThO ₂	800	62.1	76.5	91.9	1.67
	700	58.6	73.6	88.5	1.67
CoO-UO ₂	800	52.1	72.3	87.8	1.65
	700	40.0	64.6	81.8	1.58

(reduced at 500°C) and NiO-TiO₂ (reduced at 800°C) catalysts are deactivated in the process very fast (Fig.3.5.1).

The time-on-stream activity/selectivity of the reduced NiO-SiO₂ and NiO-TiO₂ catalysts is shown in Fig.3.5.1. For both the catalysts, the conversion and selectivity are decreased very markedly with increasing the time-on-stream. The carbon deposited on these catalysts was much less than that deposited on the NiO-ThO₂ catalyst. No filamental carbon growth was observed on these catalysts. Hence, the deactivation of these catalysts is expected not because of the carbon deposition but due a strong chemical interaction between nickel and SiO₂ or TiO₂ at the high reaction temperature (800°C). Further studies are necessary for understanding the cause of catalyst deactivation for both the cases.

The performance of the NiO and NiO-CoO containing catalysts (reduced at 500°C by H₂) in the oxidative conversion of methane to syngas is in the following order :

For NiO containing catalysts: NiO-ThO₂>NiO-UO₂>NiO-ZrO₂>>NiO-SiO₂>>NiO-TiO₂

For NiO-CoO containing catalysts : NiO-CoO-ThO₂ > NiO-CoO-ZrO₂ > NiO-CoO-UO₂.

Thus, among the different metal oxide supports used in the Ni or the Co- containing catalysts, the ThO₂ is the best choice.

Results showing the performance (at different temperatures) of the reduced NiO-ThO₂ and NiO-CoO-ThO₂ catalysts are given in Figure-3.5.2. As expected, both the conversion and selectivity in the process over these catalysts are increased with increasing the temperature. At 800°C, the conversion of methane over reduced NiO-ThO₂ catalyst is 94.5% with CO and H₂ selectivity of >96%. Whereas, at the same temperature, the conversion of methane over the reduced NiO-CoO-ThO₂ catalyst is 87% with 95% CO selectivity and 90% H₂ selectivity. Although, latter catalyst shows somewhat lower activity and selectivity, its performance is much superior in respect to the carbon deposition during the catalytic process. A similar observation was made for the NiO-Yb₂O₃ and NiO-CoO-Yb₂O₃ catalysts (10)

The performance of the NiO-ThO₂ catalyst is comparable (slightly superior) to that of the NiO-MgO (1) and NiO-CaO (2) and NiO-Yb₂O₃ (4) catalysts. The performance of the NiO-CoO-ThO₂ catalyst is also comparable to that of NiO-CoO-Yb₂O₃ catalyst (10)

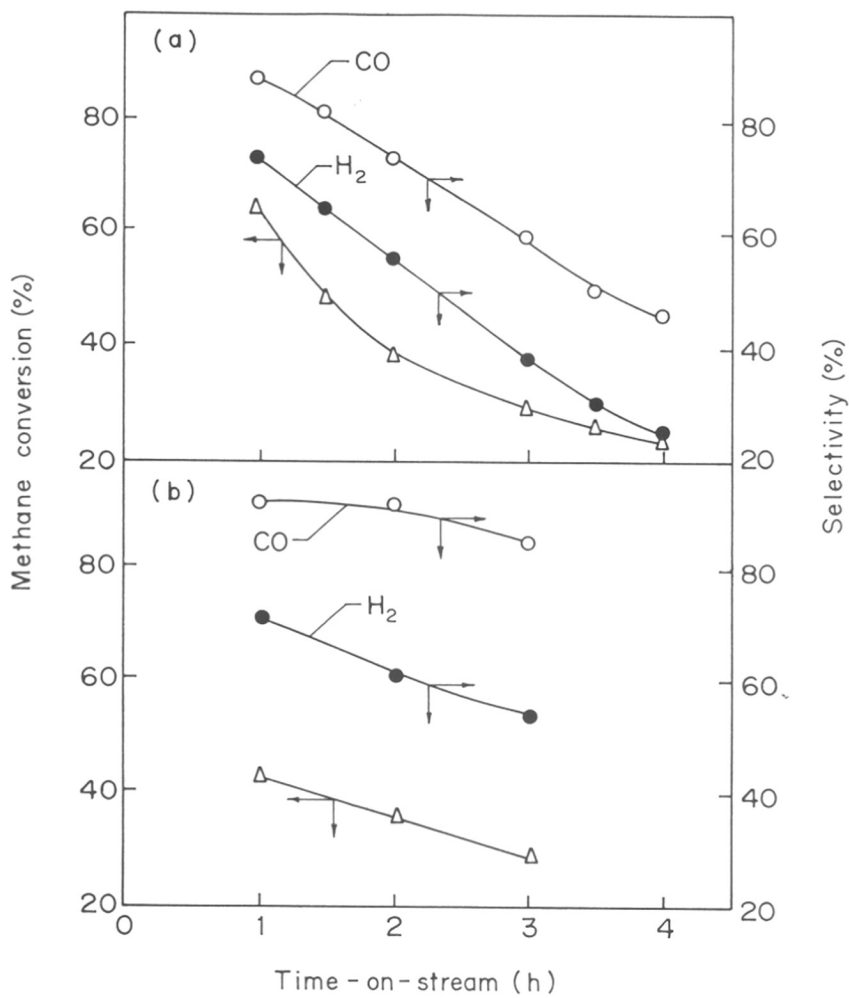


Figure 3.5.1: Influence of time-on-stream on the catalytic activity and selectivity (at 800°C) of the reduced (a) NiO-SiO₂ and (b) NiO-TiO₂ catalysts.

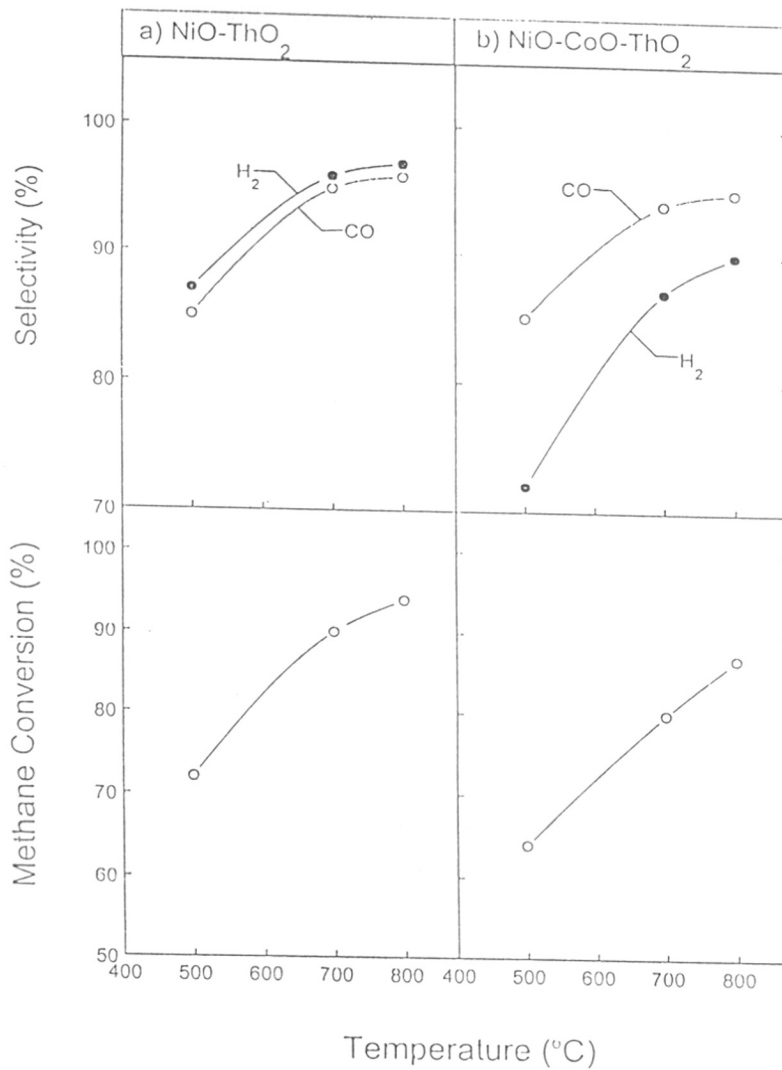


Figure 3.5.2: Influence of reaction temperature on the performance of the reduced (a) NiO-ThO₂ and (b) NiO-CoO-ThO₂ catalysts.

In the reaction over these catalysts, CO and H₂ are expected as primary products, as per the reaction mechanism suggested earlier in Chapter 3.2.

Since, cobalt is a good oxidation catalyst, its addition to Ni-ThO₂ results in a decrease in the CO selectivity due to the oxidation of adsorbed CH_x species to CO₂ and H₂O. The observed decrease in the coke deposition due to the cobalt addition also seems to result mostly from the complete oxidation of the coke precursors, such as adsorbed partially hydrogenated carbon species. Earlier studies (22) showed that adsorbed dimethyl radicals are less reactive (as compared to adsorbed carbon) and lead to the formation of amorphous carbon. As compared to the NiO-CoO-ThO₂, NiO-CoO-MgO (Chapter 3.2) seems to be a better choice as the activity and selectivity of the later catalyst is not affected by the cobalt addition (Section 3.2.2.3).

3.5.3 CONCLUSIONS

NiO-ThO₂ catalyst with or without reduction by H₂ shows very high activity and selectivity for both H₂ and CO in the oxidative conversion of methane to syngas at extremely low contact time (GHSV = 5.2 x 10⁵.cm³.g⁻¹.h⁻¹ at STP). The Ni-ZrO₂ and Ni-UO₂ catalysts also show good performance. The carbon deposition on these catalysts in the process is drastically reduced because of the addition of cobalt to them. However, the cobalt addition results in a small decrease in both the catalytic activity and selectivity of these catalysts. The NiO-TiO₂ and NiO-SiO₂ catalysts show poor activity and selectivity in the process and are deactivated very fast, probably due to strong metal (Ni)-support (TiO₂ or SiO₂) physico-chemical interactions at the high reaction temperature.

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CHAPTER-3.6

OXIDATIVE CONVERSION OF METHANE TO SYNGAS OVER NiO/MgO SOLID SOLUTION SUPPORTED ON LOW SURFACE AREA CATALYST CARRIER

3.6.1 EARLIER LITERATURE AND OBJECTIVES OF THE PRESENT WORK

During the last 8-9 years, a number of studies on the oxidative conversion of methane to syngas using various Ni, Co and noble metal containing catalysts at different contact times ranging from a few seconds to a few milliseconds have been reported (1-3). The catalytic oxidative conversion of methane to syngas at extremely low contact times (at a few milliseconds) is of great practical importance, because of the requirement of much smaller amounts of catalyst and reactor size, as compared to the presently used steam reforming process. A number of nickel (4-13) and noble metal (14-19) containing catalysts showed high activity and selectivity in the process at such a low contact times. Because of their very high cost, the noble metal containing catalysts are less preferred. Among the nickel containing catalysts, NiO-MgO is the most preferred catalyst as it exists in the form of a solid solution which stabilizes nickel against sintering during the high temperature oxidative methane-to-syngas conversion process.

In our earlier studies (4,13), NiO-MgO catalyst showed high activity and selectivity in the process at an extremely low contact time. However, when this catalyst is directly supported on different catalyst carriers to increase its mechanical strength and thermal/hydrothermal stability, the resulting supported catalyst showed lower activity and selectivity in the process(20). But, when nickel oxide was deposited on MgO precoated low surface area macroporous catalyst carrier, the resulting supported catalyst showed comparable or even better performance in the process (21,22). This supported catalyst consisted essentially NiO-MgO solid solution on a low surface area macroporous catalyst carriers (22). It is interesting to study in details the influence of various process parameters such as time-on-stream, CH_4/O_2 feed ratio, space velocity, catalyst particle size and catalyst dilution by inert solid particles on the catalytic activity and selectivity at different temperatures of the NiO-MgO supported solid solution in the methane-to-syngas conversion process. The present work was undertaken for this purpose.

3.6.2 RESULTS AND DISCUSSION

3.6.2.1 Time-on Stream Activity/Selectivity

Results showing the time-on-stream activity and selectivity of the NiO/MgO/SA-5205 catalyst in the oxidative methane-to-syngas conversion process at 700°C and at the very low contact time ($GHSV = 5.1 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$) are presented in Fig. 3.6.1. Both the methane conversion and selectivity for CO and H₂ are increased to a small extent in the initial short period of about 0.5h and thereafter remained almost constant. However, at the higher reaction temperature (800°C), no such initial increase in the conversion and selectivity was observed; the conversion and selectivity remained constant throughout the time-on-stream activity test carried out for 15h.

The observed initial increase in the conversion and selectivity of the catalyst at the lower temperature (700°C) is expected mostly due to the reduction of more NiO (buried deep in the NiO matrix of the NiO-MgO solid solution of the catalyst) to Ni⁰ (which is responsible for the catalytic activity). At the high temperature the reduction is faster and hence accomplished in much shorter initial reaction period (<0.5h).

3.6.2.2 Influence of Space Velocity

Results in Fig. 3.6.2 show a small effect of space velocity on the conversion and selectivity for CO and H₂ for the process at 800° and 900°C. However, effect of space velocity on the conversion and selectivity at the reaction temperature of 700°C is quite pronounced. When space velocity is increased from 6000 to 5,10,000 cm³ g⁻¹ h⁻¹, its effect on the conversion and selectivity at the different temperature is as follows.

- The conversion of methane at 900°C is decreased as expected but to a small extent and that at 700° and 800°C is passed through a minimum; the minimum is more pronounced at 700°C
- The H₂ selectivity at 900°C decreased to a very small extent and that at 800°C is increased but that at 700°C remained almost the same.
- The CO selectivity at 900°C is decreased to a small extent but that at 800°C and 700°C is passed through a minimum, the minimum is more pronounced at 700°C.

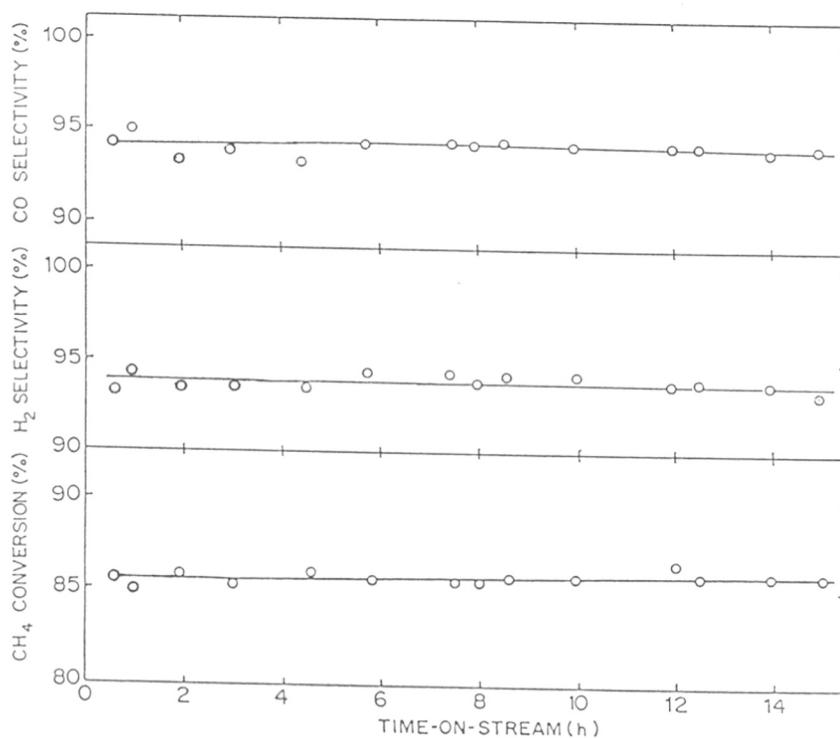


Fig. 3.6.1: Time-on-stream activity and selectivity of NiO/MgO/SA-5205 catalyst in the oxidative conversion of methane to syngas at 700°C (Feed = 66.0 mol% CH₄ and 34.0 mol% O₂, GHSV = 5.1 x 10⁵ cm³ g⁻¹ h⁻¹).

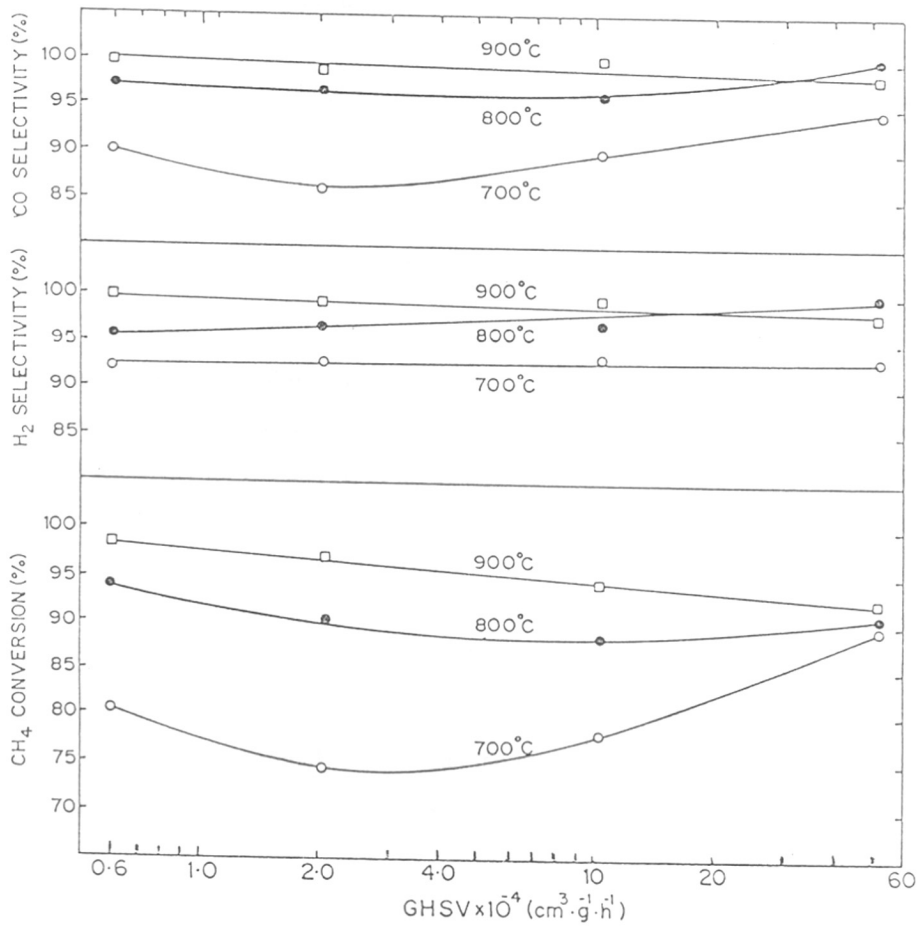


Fig. 3.6.2: Effect of space velocity on the methane conversion activity and selectivity for CO and H₂ of NiO/MgO/SA-5205 catalyst at different temperatures (feed = 64.5 mol% CH₄ and 35.5 mol% O₂).

The observed effect of GHSV on the conversion and selectivity at the different temperatures indicates the possibility of the reaction is controlled by heat transfer, particularly at lower temperatures (700° and 800°C). At the higher temperature (900°C), the selectivity for CO and H₂ is very high (above 98%) and hence heat produced in the reaction is much smaller than that at the lower temperatures (700° and 800°C) at which the CO and H₂ selectivities are lower. At the lower temperatures, the heat produced is more because of the highly exothermic total combustion reaction ($\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 191.5 \text{ kcal. mol}^{-1}$) as the CO selectivity is lower than that at 900°C. Thus, higher heat of reaction combined with high conversion ($\geq 75\%$) results in a temperature increase at the catalyst surface with increasing the space velocity, causing the observed increase in the conversion and CO selectivity.

3.6.2.3 Influence of CH₄/O₂ Ratio in Feed

Results showing the effect of CH₄/O₂ ratio (varied from 1.8 to 8.0) on the conversion activity and selectivity for CO and H₂ of the catalyst at different temperatures (600°-800°C) are presented in Fig. 3.6.3. The conversion, H₂ selectivity and CO selectivity at all the temperatures are decreased with increasing the CH₄/O₂ ratio.

The observed decrease in the conversion is expected because of the lower amounts of oxygen than that required for the reaction stoichiometry (reaction 1) is available for the reaction. The decrease in the selectivity for CO and H₂ may be due to decrease in the temperature at the catalyst surface (which is generally higher than the measured temperature for any exothermic catalytic reaction) as the conversion is decreased, with increasing the CH₄/O₂ ratio.

3.6.2.4 Influence of Catalyst Dilution

Results of Fig. 3.6.4 clearly show that the catalyst dilution by inert solid particles (having size same as that of the catalyst) has a strong effect on both the conversion and selectivity in the process. Both the conversion and selectivity are decreased because of the catalyst dilution (diluent/catalyst weight ratio = 4.0) at the different temperatures (500°-800°C). Because of the catalyst dilution, a more area for the heat transfer from the reactor for the same amount of catalyst is available for the removal of heat produced by the reaction. The observed

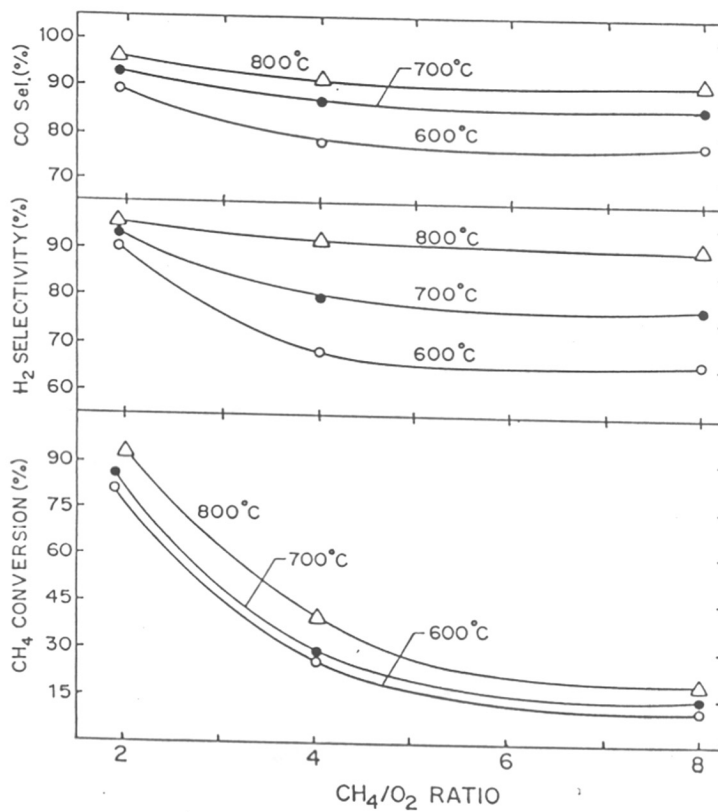


Fig. 3.6.3: Influence of CH₄/O₂ on the methane conversion activity and selectivity for CO and H₂ of NiO/MgO/SA-5205 catalyst at different temperatures GHSV = 5.1 x 10⁵ cm³ g⁻¹ h⁻¹).

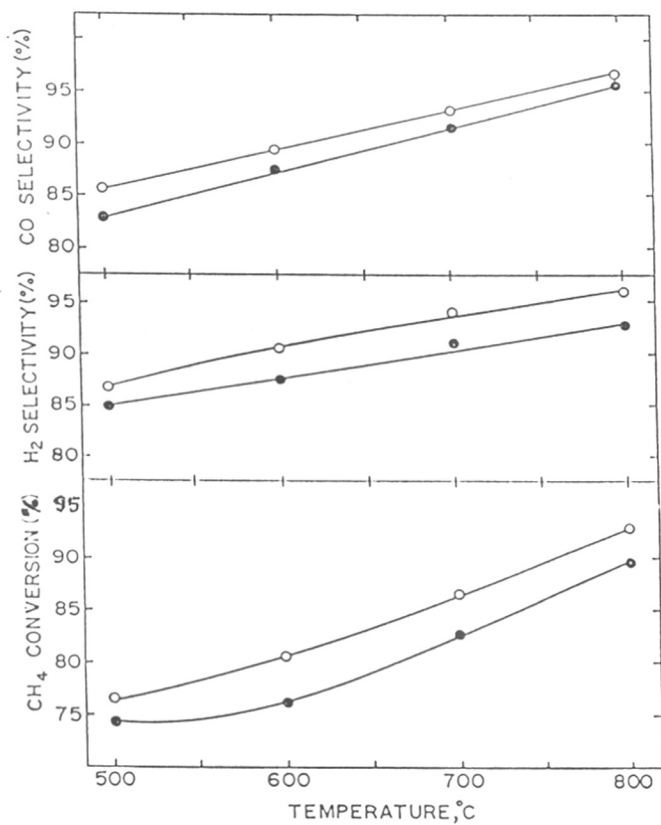


Fig. 3.6.4: Effect of catalyst dilution on the activity and selectivity of NiO/MgO/SA-5205 catalyst at different temperatures (feed = 64.5 mol% CH₄ and 35.5 mol% O₂, GHSV = 5.1 × 10⁵ cm³ g⁻¹ h⁻¹). [● - with catalyst dilution (diluent/catalyst weight ratio 4.0 and ○ - without catalyst dilution)].

catalyst dilution effect on both the conversion and selectivity indicates that oxidative methane-to-syngas conversion reaction over catalyst is influenced by the heat transfer from the catalyst.

3.6.2.5 Effect of Catalyst Particle Size

Results in Table-3.6.1 show a mild effect of catalyst particle size on the conversion and selectivity in the process at 700° and 800°C. The observed small decrease in the conversion with increasing the particle size indicates that the oxidation reaction is influenced to some extent by the intraparticle mass transfer.

Table 3.6.1. Influence of particle size of the NiO/MgO/SA-5205 catalyst on its methane conversion activity and H₂/CO ratio in the oxidative conversion of methane to syngas in the presence of CO₂ and steam at 700°C and 800°C [Feed : 60.2 mol% CH₄, 27.4 mol% O₂, 6.7 mol% CO₂ and 5.7 mol% H₂O; GHSV = 41,500 cm³ g⁻¹ h⁻¹]

Particle size (mesh)	CH ₄ conversion (%)	Selectivity (%)	
		CO	H ₂
<u>Reaction temperature: 700°C</u>			
22-30	89.7	93.0	92.1
30-52	91.1	93.2	92.3
52-70	93.2	95.7	94.5
<u>Reaction temperature : 800°C</u>			
22-30	93.0	94.8	94.1
30-52	93.6	95.1	95.9
52-70	96.7	97.1	97.5

The selectivity for both H₂ and CO is also decreased to a small extent with increasing particle size. It seems that because of a combined effect of heat and mass transfer, the observed effect of particle size on the conversion and selectivity is small.

3.6.3 CONCLUSIONS

The studies on the influence of time-on-stream, space velocity, CH_4/O_2 feed ratio, catalyst dilution and catalyst particle size on the conversion and selectivity at different temperatures in the oxidative conversion of methane to syngas over the NiO/MgO/SA-5205 catalyst lead to the following important conclusions.

- The catalyst shows no sign of deactivation when on the time-on-stream for 15h.
- The effect of space velocity on the conversion and selectivity is small and, moreover, depends on the reaction temperature.
- Both the conversion and selectivity are decreased with increasing the CH_4/O_2 ratio in the feed.
- Because of the catalyst dilution by inert solid particles, both the conversion and selectivity are decreased.
- The conversion and selectivity are increased to a small extent with increasing catalyst particle size
- The observed effects of the space velocity, CH_4/O_2 feed ratio, catalyst dilution and catalyst particle size indicate that the catalytic reaction is influenced by both the heat and mass transfer processes, particularly at the lower temperatures.

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PART-IV

**CATALYTIC STEAM AND / OR CO₂ REFORMING WITH OR WITHOUT
SIMULTANEOUS OXIDATIVE CONVERSION OF METHANE TO
SYNGAS**

CHAPTER-4.1

CO₂ REFORMING, SIMULTANEOUS CO₂ AND STEAM REFORMING AND OXY-CO₂ OR STEAM REFORMING OF METHANE OVER NiO-MgO SOLID SOLUTION

4.1.1. EARLIER LITERATURE AND OBJECTIVES OF THE PRESENT WORK

In our earlier studies (1, 2) and chapters 3.1 and 3.2, NiO-MgO catalyst showed high activity/selectivity and productivity in the oxidative conversion of methane to syngas. The high activity of nickel in this catalyst is attributed to the formation of solid solution of NiO in MgO, and thereby, the degree of NiO reduction is low. On the reduction of NiO-MgO solid solution, the outermost Ni^o atoms nucleate to form fine metal particles but some, which lie deeper, remain isolated in the MgO matrix either as Ni^o or as 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^o) which are at the surface but not fully exposed (3). It is, therefore, interesting to carry out further work on the NiO-MgO solid solution for studying its performance in the oxidative conversion of methane to syngas, simultaneous steam and CO₂ reforming of methane and also in the simultaneous exothermic oxidative conversion and endothermic steam or CO₂ reforming of methane involving the coupling of exothermic and endothermic reactions. This investigation was undertaken for this purpose.

4.1.2 RESULTS AND DISCUSSION

4.1.2.1 CO₂ Reforming, Simultaneous CO₂ and Steam Reforming of Methane to Syngas

The catalyst shows high activity and H₂ selectivity even in CO₂ reforming alone (Table-4.1.1). At 800°C, a complete conversion of methane with 96% selectivity for H₂ (H₂/CO product ratio = 0.9) can be obtained at high space velocity ($3.9 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$) for CH₄/CO₂ ratio of 0.8. The lower H₂ selectivity at the lower CH₄/CO₂ feed ratio is expected because of the reverse water gas reaction (Reaction 3).

Table 1 : Results of the CO₂ reforming of methane at different CH₄/CO₂ ratios at 800°C (space velocity = 3.9 x 10⁴ cm³ g⁻¹ h⁻¹)

	CH ₄ /CO ₂ ratio		
	0.8	0.9	1.0
CH ₄ conversion (%)	100.0	99.5	96.8
CO ₂ conversion (%)	92.5	96.7	98.0
H ₂ selectivity (%)	96.0	99.0	99.5
H ₂ /CO ratio	0.90	0.95	0.99

Results of the simultaneous CO₂ and steam reforming of methane to syngas over the catalyst at different temperatures for the CH₄/O₂ and CH₄/H₂O feed ratios of 1.8 and 2.0, respectively, and space velocity of 36,120 cm³ g⁻¹ h⁻¹ are given in Fig.4.1.2. With the increase in the temperature, the conversion of all the reactants (viz. CH₄, CO₂ and H₂O) is increased and the H₂/CO product ratio is decreased. At or above 800°C, the conversion of methane is very high (>95.0%) and the H₂/CO ratio is between 1.5 and 1.6, which is suitable for the Fischer-Tropsch synthesis process. The H₂/CO ratio can be varied by manipulating the H₂O/CO₂ feed ratio (7). The decrease in H₂/CO ratio indicates that the CO₂ reforming (Reaction 2) becomes more and more predominant over the steam-reforming (Reaction 4).

In the simultaneous steam and CO₂ reforming of methane, there is no formation of any side product and hence the selectivity for the desired products (H₂ and CO) is 100%, as long as the net conversion of water and CO₂ is greater than or equal to zero.

4.1.2.2 Oxy-CO₂ Reforming of Methane to Syngas

Results showing no significant effect of the process time, at least for 14h, on the conversion of CH₄, CO₂ and O₂, selectivity for H₂ and H₂/CO product ratio in the simultaneous oxidative conversion and CO₂ reforming of methane over the catalyst at 800°C are presented in Fig. 4.1.1. The effect of temperature on the conversion, selectivity and H₂/CO product ratio and net heat (ΔHr) of reactions involved in the oxy-CO₂ reforming process is shown in Fig. 4.1.3. The conversion of O₂ in all the cases was 100%. The net heat of reaction (ΔHr) is estimated by

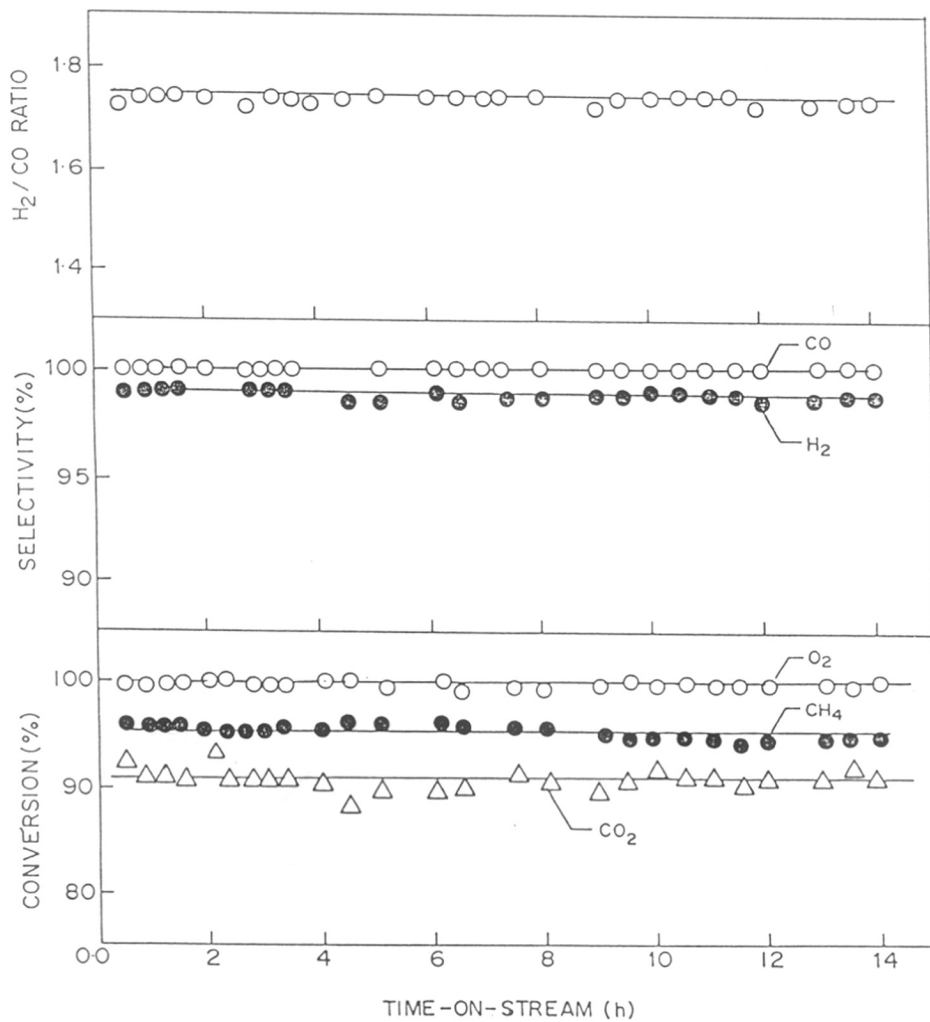


Fig. 4.1.1: Time-on-stream activity of the NiO-MgO catalyst in the oxy-CO₂ reforming of methane to syngas at 800°C ($\text{CH}_4/\text{O}_2 = 2.5$, $\text{CH}_4/\text{CO}_2 = 3.5$, $\text{GHSV} = 43,860 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$).

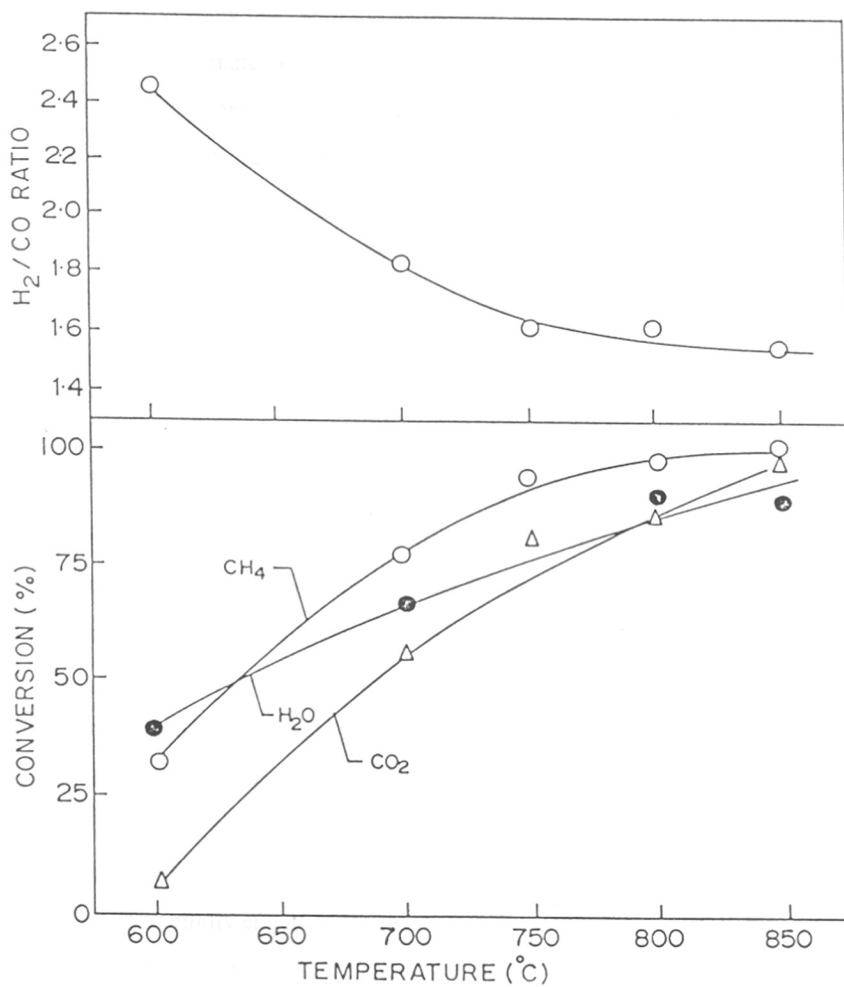


Fig.4.1.2: Effect of temperature on the activity and H_2/CO product ratio of the NiO-MgO catalyst in the simultaneous steam and CO_2 -reforming of methane ($CH_4/O_2 = 1.8$, $CH_4/H_2O = 2.0$, GHSV = $36,120 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$)

subtracting the heat of formation (at the process temperature) of the components in the feed from that of the components in the product stream.

The results (Fig. 4.1.3) show that, with the increase of temperature (from 700° to 850°C) in the oxy-CO₂ reforming of methane, a) the conversion of methane and CO₂ is increased, the increase being larger in the CO₂ conversion, b) the selectivity for H₂ is increased but to a small extent, c) the H₂/CO ratio is decreased, and d) the net heat of reaction (ΔHr) is increased indicating a decrease in process exothermicity or an increase in the process endothermicity.

In the oxy-CO₂ reforming process, both the exothermic conversion of methane,



and endothermic CO₂ reforming of methane,



occur simultaneously along with a side reverse water gas reaction,



The H₂ selectivity is lower than 100% because of the reverse water gas reaction (Reaction 3). The increase in the H₂ selectivity with the temperature indicates that the reverse water gas reaction occurs to a small extent at the higher temperatures. However, the CO₂ reforming reaction is favored more and more at the higher temperature. The observed decrease in the H₂/CO product ratio and increase in the value of ΔHr (or increase in the process endothermicity) with increasing the temperature are the result of a higher methane conversion by the CO₂ reforming. Thus, the reaction temperature is an important process variable for controlling the process exothermicity or endothermicity; the process can be made mildly exothermic, thermoneutral or mildly endothermic by manipulating the reaction temperature.

It may be noted that, in the process, the selectivity for CO (based on methane) is always 100% as long as the net conversion of CO₂ is greater than or equal to zero. The catalyst shows high activity (CH₄ conversion ≥ 95%) and selectivity for H₂ (> 95%) in the oxy-CO₂ reforming process (at ≥ 800°C) at a high space velocity (4.9 × 10⁴ cm³ g⁻¹ h⁻¹).

4.1.2.3 Oxy-steam Reforming of Methane to Syngas

Results showing the influence of CH₄/O₂ feed ratio (when CH₄/H₂O ratio in feed = 1.44) at two different temperatures (700° and 800°C) on the conversion, selectivity, H₂/CO product

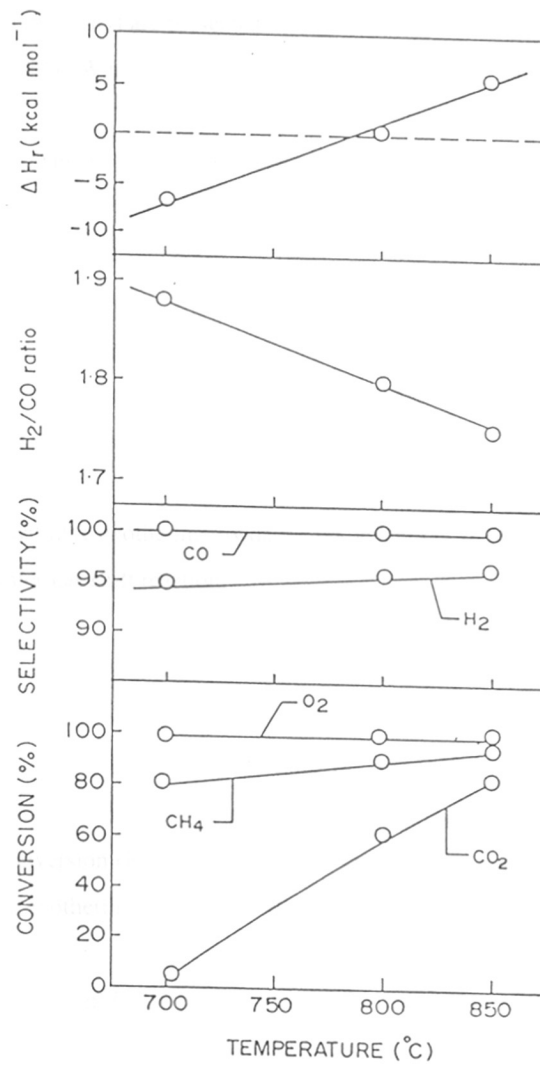


Fig. 4.1.3: Effect of temperature on the performance of the NiO-MgO catalyst in the oxy-CO₂ reforming of methane to syngas ($\text{CH}_4/\text{O}_2 = 2.2$, $\text{CH}_4/\text{CO}_2 = 7.3$, $\text{GHSV} = 49,200 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$).

ratio and net heat of reactions (ΔH_r) in the oxy-steam reforming of methane to syngas at high space velocity ($40,600 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$) are presented in Fig. 4.1.4. In this case also the conversion of O_2 in all the runs was 100%. When the CH_4/O_2 feed ratio is increased, the process is influenced as follows :

- the conversion of methane is decreased but that of water is increased.
- the selectivity for CO at 700°C is decreased markedly and that at 800°C is also decreased but only to a very small extent.
- the H_2/CO ratio is increased.
- the value of ΔH_r is increased markedly.

These observations indicate that, in the oxy-steam reforming process, the endothermic steam reforming of methane,



occurs simultaneously with the exothermic oxidative conversion of methane to syngas (Reaction 1), along with a side water gas shift reaction,



The CO selectivity in the process is much less than 100% and this is due to the side water gas shift reaction (Reaction 5), depending upon the temperature and CH_4/O_2 feed ratio. The increase in the H_2/CO ratio and also in the value of ΔH_r with increasing the CH_4/O_2 ratio indicates that the methane conversion by the steam reforming reaction (Reaction 4) relative to that by the oxidative conversion (Reaction 1) is increased with decreasing the O_2 concentration in the feed. The process exothermicity or endothermicity can thus be controlled by manipulating the CH_4/O_2 ratio in the feed.

In the oxy-steam reforming process, the selectivity for H_2 (based on methane) is always 100% as long as the net conversion of water is greater than or equal to zero.

4.1.3 CONCLUSIONS

The NiO-MgO solid solution shows high catalytic activity and selectivity not only in the oxidative conversion of methane to syngas but also in the oxy- CO_2 reforming, and oxy-steam reforming, CO_2 reforming and simultaneous CO_2 and steam reforming of methane to syngas. In the oxy-steam and oxy- CO_2 reforming processes, the exothermic oxidative conversion and

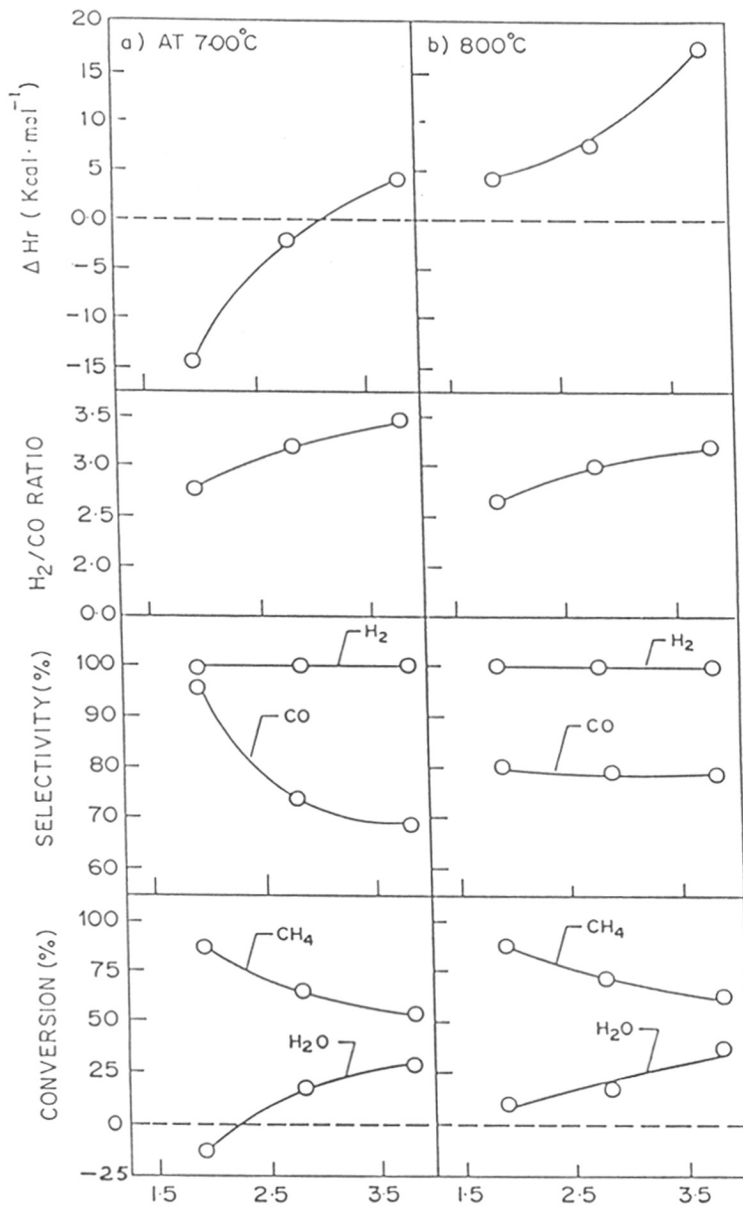


Fig. 4.1.4: Effect of CH₄/O₂ ratio in the feed on the performance of the NiO-MgO catalyst in the oxy-steam reforming of methane at a) 700° and b) 800°C (CH₄/H₂O ratio in the feed = 1.44, GHSV = 49,200 cm³ g⁻¹ h⁻¹).

endothermic steam or CO₂ reforming reactions are coupled, making the process highly energy efficient and also safe to operate.

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CHAPTER 4.2

CO₂ REFORMING, OXY-CO₂ REFORMING AND OXY-STEAM REFORMING OF METHANE TO SYNGAS OVER NiO-CoO-MgO SOLID SOLUTION

4.2.1 EARLIER LITERATURE AND THE OBJECTIVES OF THE PRESENT WORK

Our earlier studies revealed that both the supported (1) and unsupported (2) NiO-MgO solid solution shows high activity (methane conversion > 85%) and selectivity (>90% for both CO and H₂) in the oxidative conversion of methane to CO and H₂ at a very low contact time (space velocity of about $5.0 \times 10^5 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$). CoO-MgO solid solution (3) also showed high catalytic activity but relatively lower selectivity in the process. However, our recent studies (4) indicated that the addition of cobalt to NiO-Yb₂O₃, NiO-ZrO₂ and NiO-ThO₂ catalysts causes a drastic reduction in the rate of carbon formation in the oxidative conversion of methane to syngas at a very low contact time. The high activity of NiO-MgO is attributed to the formation of solid solution of NiO in MgO. On the reduction of the NiO-MgO solid solution by H₂ or during the methane-to-syngas conversion process, the outermost Ni⁰ atoms nucleate to form fine metal particles but some, which lie deeper, remain isolated in the MgO matrix either as Ni⁰ 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 (Ni⁰) which are at the surface but not fully exposed (5). Cobalt oxide also forms a solid solution with MgO at all concentrations (6). Since both NiO and CoO can form a solid solution with MgO, it is interesting to study the performance of NiO-CoO-MgO solid solution in the methane to syngas conversion process. Our earlier studies (Chapter 3.2) indicated that the addition of cobalt to NiO-MgO catalyst has no significant effect on the catalytic activity/selectivity in the oxidative conversion of methane to syngas. The present investigation was undertaken with the objective of studying activity and selectivity for CO and H₂ of CoO-NiO-MgO (Co : Ni : Mg = 0.5 : 0.5 : 1.0) solid solution in various methane-to-syngas conversion reactions (viz., CO₂ reforming, oxidative conversion, Oxy-CO₂ reforming, and Oxy-steam reforming reactions) at different reaction conditions.

4.2.2 RESULTS AND DISCUSSION

Oxidative Conversion of Methane to Syngas

4.2.2.1. CO₂ Reforming of Methane to Syngas

Results showing the influence of time-on-stream activity on the conversion, H₂ selectivity and pressure drop across the catalyst bed in the reactor (which is a measure of filamental carbon deposition on the catalyst in the process) in the CO₂ reforming of methane to CO and H₂ over the NiO-MgO and NiO-CoO-MgO catalysts are presented in the Fig. 4.2.1. In case of the NiO-MgO catalyst, there was sharp increase in the pressure drop with increasing the time-on-stream, indicating rapid deposition of filamental carbon on the external surface of the catalyst. However, the decrease in the conversion of CO₂ and CH₄ and selectivity for H₂ in the process is small. This indicates that carbon deposited is porous in nature and had only a small catalyst deactivating effect. However, since the increase in the pressure drop is fast it was not possible to continue the process for a longer period (above 3h). On the contrary, in case of the NiO-CoO-MgO catalyst there was a very small increase in the pressure drop, even after the time-on-stream of 5h, and more over, there was no significant change in the conversion and selectivity (Fig. 4.2.1b).

A comparison of the performance of two catalysts indicates that because of the addition of CoO to or the replacement of half of the NiO from the NiO-MgO catalyst, the deposition of filamental carbon on the catalyst is drastically reduced at the expense of a small catalytic activity.

4.2.2.2. Oxy-CO₂ Reforming of Methane to Syngas

Results in Fig. 4.2.2 reveal that the activity and selectivity and the pressure drop across the catalyst bed in the oxy-CO₂ reforming of methane over the NiO-CoO-MgO catalyst are not changed at least for the time-on-stream of 10h. This shows that there is little or no carbon deposition on the catalyst in the process and hence there is no catalytic deactivation. However, in case of the NiO-MgO catalyst, the increase in the pressure drop with the time-on-stream was so sharp (Fig. 4.2.2) that it was not possible to carry out the oxy-CO₂ reforming process over the

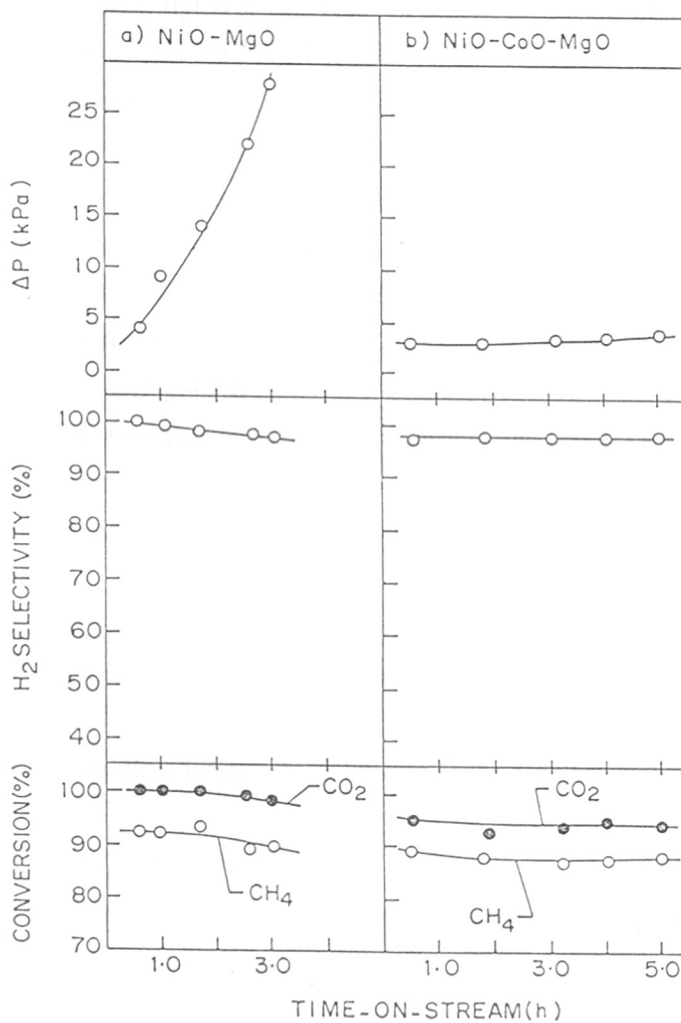


Fig. 4.2.1.:Variation of conversion, selectivity and pressure drop across the reactor in the CO_2 reforming of methane over NiO-MgO and NiO-CoO-MgO catalysts at $850^\circ C$ (CH_4/CO_2 ratio in feed = 1.1, GHSV = $13,500 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$).

catalyst even for a period of 15 min. during this period the pressure drop was increased from 5 kPa to 30 kPa due to the formation of carbon filaments between the catalyst particles, drastically reducing the catalyst bed porosity.

Results showing the influence of temperature and reactant ratios (CH_4/O_2 and CH_4/CO_2) on the conversion, selectivity, H_2/CO product ratio and also on the net heat of reaction (ΔHr) in the process are presented in Figs. 4.2.3 and 4.2.4. The net heat of reaction (ΔHr) for the overall process is estimated by subtracting the heat of formation (at the process temperature) of the components in the feed from that of the components in the product stream.

When reaction temperature is increased (Fig. 4.2.3), the conversion of CH_4 and CO_2 , H_2 selectivity and net heat of reaction (ΔHr) or process endothermicity are increased and the H_2/CO product ratio is decreased. Whereas, the increase in the CH_4/O_2 ratio or a corresponding decrease in CH_4/CO_2 ratio, while keeping the $\text{CH}_4/(\text{O}_2+0.5\text{CO}_2)$ feed ratio constant, has following effects on the process performance (Fig. 4.2.4) :

- * The conversion of methane is decreased to a small extent, that of O_2 is unaffected but that of CO_2 is increased markedly.
- * The H_2 selectivity is decreased to a small extent and consequently the H_2/CO ratio is also decreased.
- * The net heat of reaction (ΔHr) is increased markedly; the process was exothermic for the low CH_4/O_2 ratio (2.05) but became more and more endothermic for the higher CH_4/O_2 ratios.

The above observations indicate the occurrence of the endothermic CO_2 reforming of methane,



simultaneously with the exothermic oxidative conversion of methane to CO and H_2 ,



over the catalyst. The observed H_2 selectivity lower than 100% is because of the side reverse water gas reaction,



The - ve conversion of CO_2 at the low temperature (Fig. 4.2.3) indicates that there is a net CO_2 formation in the process due to combustion of methane,

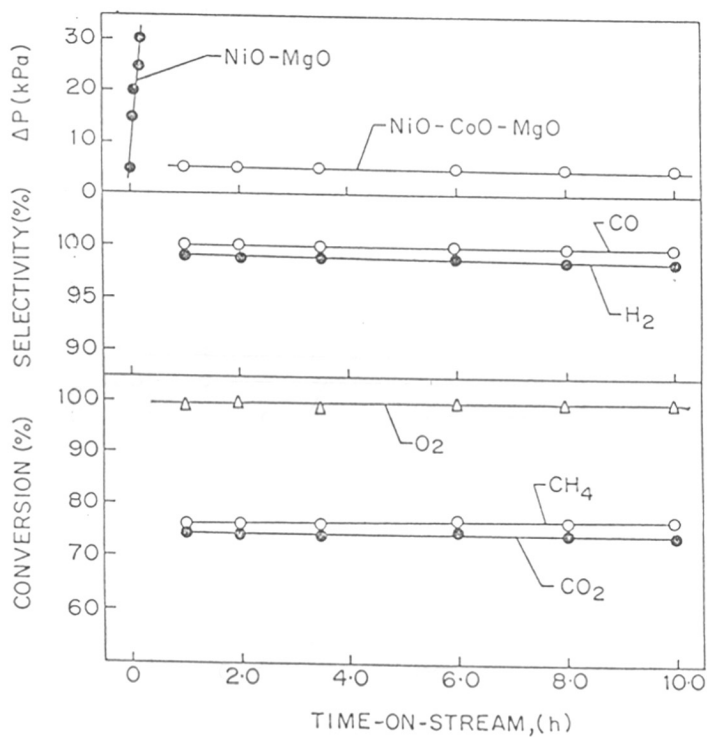


Fig.4.2.2.: Time-on-stream activity/selectivity of the NiO-CoO-MgO catalyst in the oxy-CO₂ reforming of methane to syngas at 800°C ($\text{CH}_4/\text{O}_2 = 2.5$, $\text{CH}_4/\text{CO}_2 = 3.4$ and $\text{GHSV} = 4.5 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$).

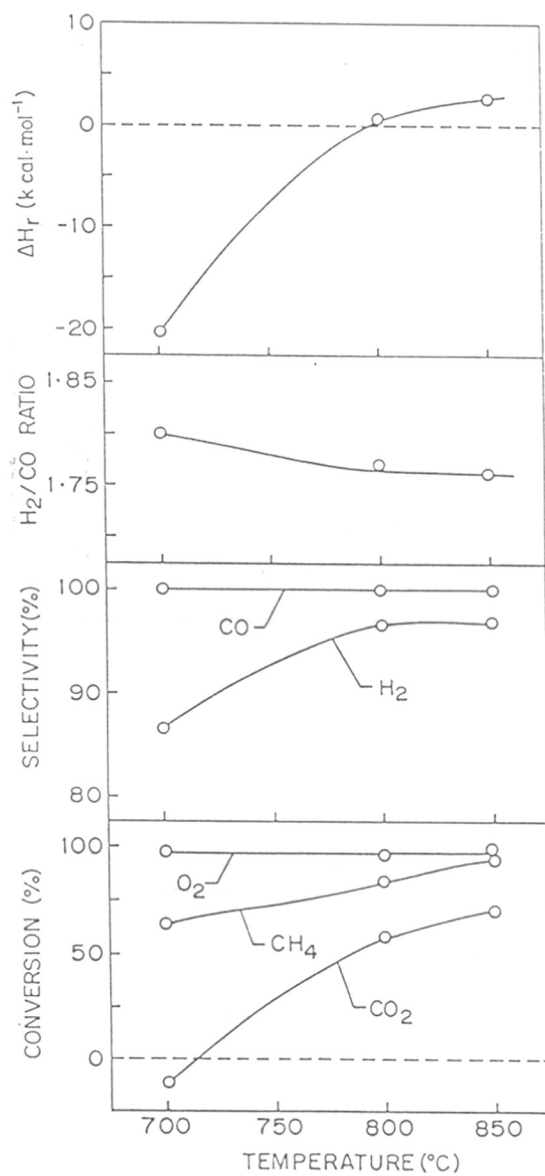


Fig. 4.2.3: Effect of temperature on the oxy-CO₂ reforming of methane over the NiO-CoO-MgO catalyst ($\text{CH}_4/\text{O}_2 = 2.2$, $\text{CH}_4/\text{CO}_2 = 7.2$ and $\text{GHSV} = 4.5 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$).

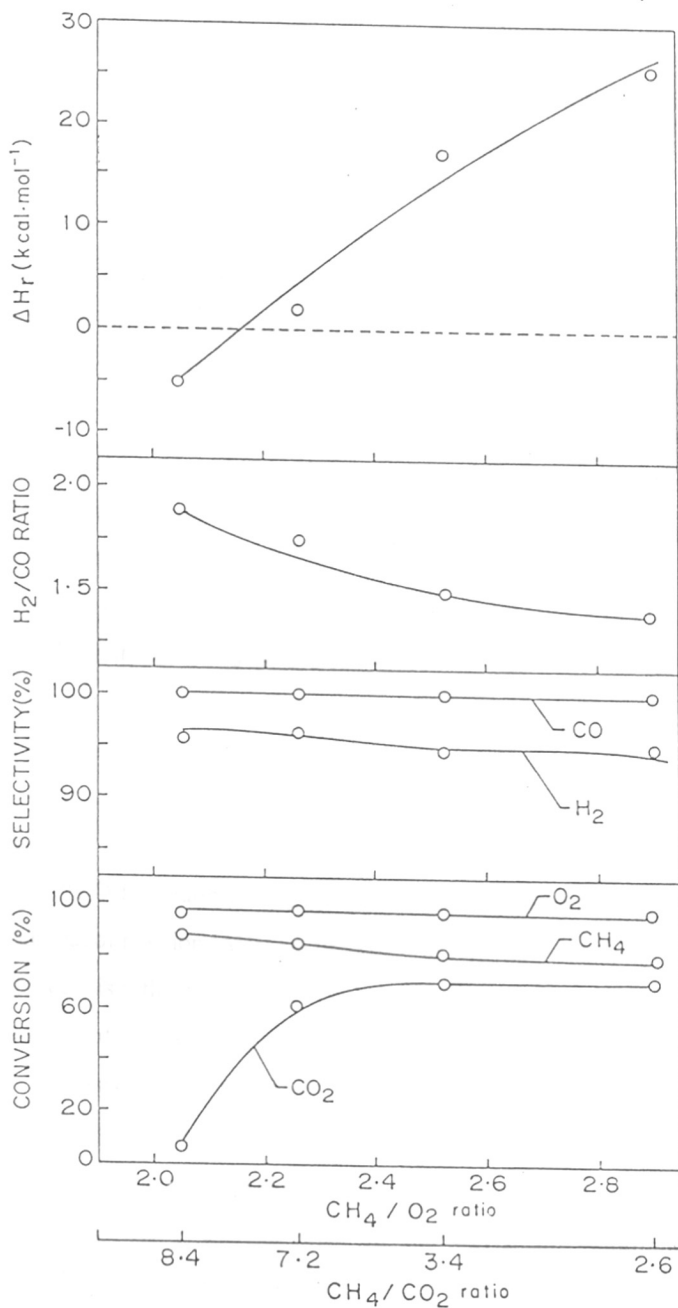
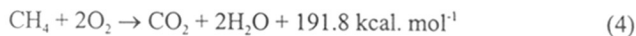


Fig. 4.2.4: Effect of CH_4/O_2 or CH_4/CO_2 ratio on the oxy- CO_2 reforming of methane over the NiO-CoO-MgO catalyst at 800°C [$\text{CH}_4/(\text{O}_2+0.5\text{CO}_2) = 1.9$, $\text{GHSV} = 4.5 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$].



making the process more exothermic. Because of the coupling of the exothermic and endothermic reactions (Reactions 1 and 2), the heat produced or absorbed in the process (or process exothermicity or endothermicity) can be controlled by manipulating the temperature or CH_4/O_2 feed ratio; the heat produced is decreased with increasing the temperature or CH_4/O_2 feed ratio. Thus, by manipulating the reaction temperature and/or CH_4/O_2 ratio, the process can be made mildly exothermic, thermoneutral or mildly endothermic.

Figure 4.2.5 shows the effect of space velocity on the conversion, selectivity and H_2/CO product ratio in the process over the NiO-CoO-MgO catalyst at 800°C . The effect of space velocity on the conversion of O_2 and CH_4 , H_2 selectivity and H_2/CO product ratio is small but the effect on the CO_2 conversion is strong, particularly at the higher space velocities because of the lower rate of the CO_2 reforming.

In the oxy- CO_2 reforming process, as long as the conversion of CO_2 is greater than or equal to zero, the selectivity for CO is always 100%.

4.2.2.3. Oxy-Steam Reforming of Methane to Syngas

Results of the oxy-steam reforming of methane to syngas over the NiO-CoO-MgO catalyst at two different temperatures (700° and 800°C), showing the influence of CH_4/O_2 feed ratio (when the $\text{CH}_4/\text{H}_2\text{O}$ feed ratio is 1.5) on the conversion, selectivity, H_2/CO product ratio and also on the net heat of reaction (ΔH_r) are presented in Fig.4.2.6. When the CH_4/O_2 feed ratio is increased, the process is influenced as follows.

- * The conversion of methane is decreased to a small extent but that of water is increased markedly. Whereas, the conversion of O_2 in all cases was complete.
- * The CO selectivity is increased and consequently H_2/CO product ratio is decreased.
- * The value of ΔH_r is increased markedly.

The above observations indicate that, in the oxy-steam reforming process, the endothermic steam reforming of methane,



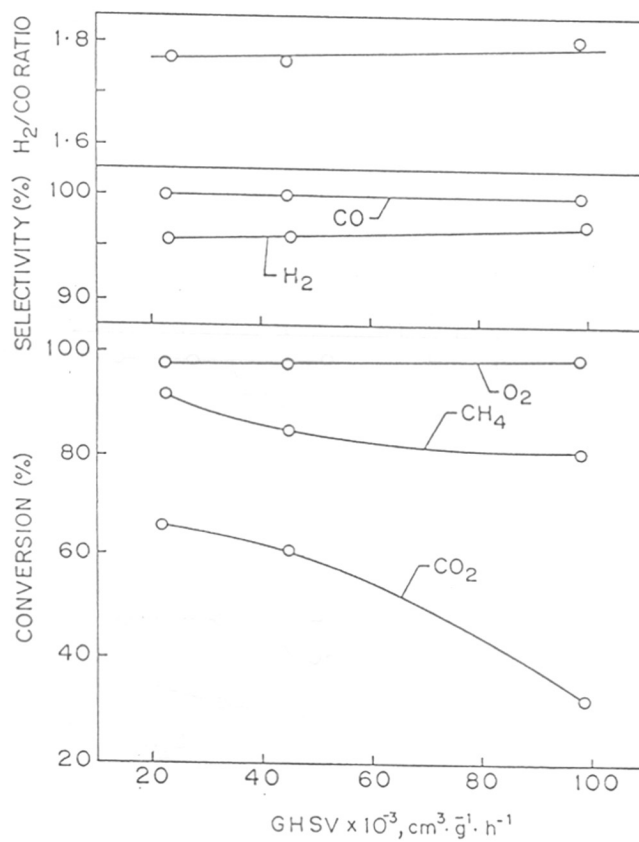


Fig. 4.2.5.: Effect of GHSV on the oxy- CO_2 reforming of methane over the NiO-CoO-MgO catalyst at 800°C ($\text{CH}_4/\text{O}_2 = 2.2$, $\text{CH}_4/\text{CO}_2 = 7.3$).

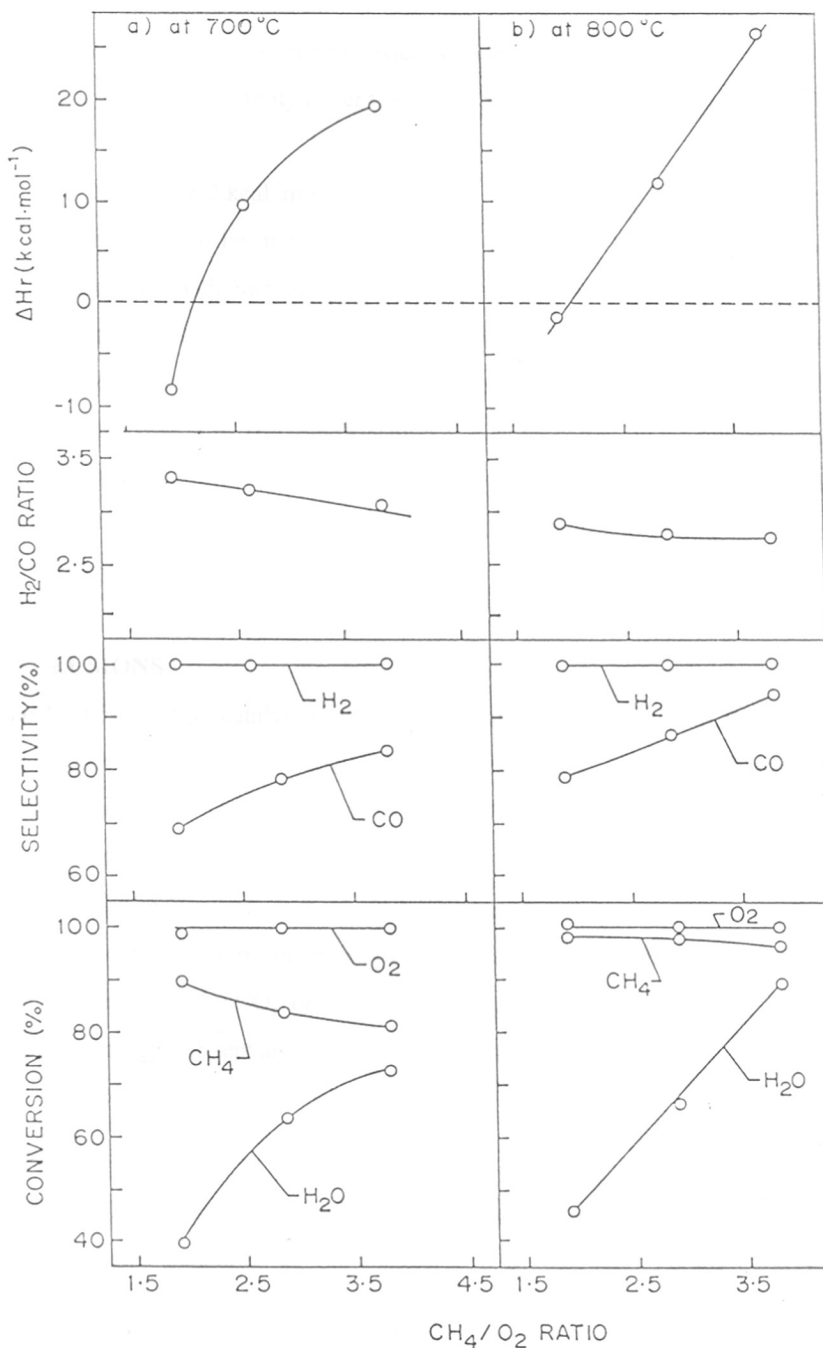


Fig. 4.2.6: Oxy-steam reforming of methane to syngas over the NiO-CoO-MgO catalyst at 700° and 800°C for different CH₄/O₂ ratios. (CH₄/H₂O = 1.5, GHSV = 9500 cm³ g⁻¹ h⁻¹).

occurs simultaneously with the exothermic oxidative conversion of methane to syngas (Reaction 2). Also, the observed CO selectivity lower than 100% indicates occurrence of the side water gas shift reaction,



This side reaction seems to be more predominant at the lower CH_4/O_2 ratio because the CO selectivity is increased with increasing the CH_4/O_2 ratio. The selectivity for H_2 (based on methane) in this process is 100% as long as the conversion of water is greater than or equal to zero. The increase in the value of ΔH_r with increasing CH_4/O_2 ratio indicates that the methane conversion by steam reforming reaction (Reaction 5) relative to that by the oxidative conversion (Reaction 2) is increased with decreasing the O_2 concentration in the feed or decreasing the $\text{O}_2/\text{H}_2\text{O}$ feed ratio. Thus, the process exothermicity can be controlled by manipulating the feed ratios.

4.2.3. CONCLUSIONS

The NiO-CoO-MgO catalyst shows high activity and selectivity in the conversion of methane to syngas by the oxidative conversion, CO_2 reforming, oxy- CO_2 reforming and oxy-steam reforming reactions. The addition of CoO to NiO-MgO catalyst has beneficial effect on the process performance for eliminating or drastically reducing the formation of filamental carbon on the catalyst particularly in the process involving the CO_2 reforming of methane. In the oxy- CO_2 and oxy-steam reforming processes over this catalyst, the exothermic oxidative conversion and endothermic CO_2 or steam reforming reactions are coupled, making these processes highly energy efficient and non hazardous or safe to operate.

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CHAPTER-4.3

CO₂ REFORMING, STEAM REFORMING AND SIMULTANEOUS CO₂ AND STEAM REFORMING OF METHANE OVER Co_xNi_{1-x}O SUPPORTED ON MACROPOROUS SILICA-ALUMINA PRECOATED WITH MgO

4.3.1. EARLIER LITERATURE AND OBJECTIVES OF THE PRESENT WORK

Release of large quantities of CO₂ in the atmosphere has created a large greenhouse effect causing a global warming. Hence worldwide efforts are being made for conversion of CO₂ to useful products. One of the ways of activating CO₂ is its reaction with methane to carbon monoxide and hydrogen, commonly known as CO₂ reforming of methane. In the last few years, the research activities on the CO₂ reforming of methane have gained a lot of momentum (1). Several studies on this reaction over different catalysts, such as supported Pt group metals (2-10), Ni/MgO (6, 11), Ni/Al₂O₃ (12), Ni/MgO-CaO (13), NiO-CaO (14) and NiO/MgO/SA-5205 (15), have been reported. A rapid coke deposition on the catalyst is, however, a serious problem in the CO₂ reforming of methane, particularly when Ni-containing catalyst is used. (6, 14). CO₂ reforming simultaneously with steam reforming and/or oxidative conversion of methane over NiO-CaO (14, 16, 17), NiO-MgO (11) and LaNiO₃ (18), Ni/ALPO-5 (19) and NiO/MgO/SA-5205 (15) catalysts have also been reported earlier. The coke formation in CO₂ reforming over NiO-CaO catalyst was reduced drastically by carrying out the CO₂ reforming simultaneously with steam reforming (14) or oxidative conversion (17) of methane to syngas.

Our earlier study (20) revealed that the addition of cobalt to unsupported Ni-containing catalysts causes a drastic reduction in the carbon formation in the oxidative conversion of methane to syngas. It is, therefore, interesting to study the effect of cobalt addition to Ni-containing catalysts on carbon deposition on them in the CO₂ reforming.

In our earlier studies, NiO supported on a low surface area macroporous silica-alumina catalyst carrier precoated with MgO showed high activity and selectivity in the steam reforming, CO₂ reforming and simultaneous steam and CO₂ reforming of methane to syngas in the presence or absence of O₂ (15, 21). The present work was undertaken for studying the influence of cobalt

addition to this catalyst on its activity and selectivity and also on the filamental carbon formation in the CO₂ reforming and/or steam reforming at different process conditions.

4.3.2.RESULTS

4.3.2.1.Catalyst Characterization

Results showing the influence of Co/Ni ratio in the catalyst on surface area are given in Table 4.3.1 The surface area is decreased appreciably with increasing the Co/Ni ratio in the catalyst.

Figure 4.3.1 shows curves for the TPR (by H₂) from 100° to 900°C of the catalyst with different Co/Ni ratios (0.05 - 1.0). The TPR of the catalyst without cobalt (NiO/MgO/SA-5205) is given earlier (15). The TPR curves are quite similar to that observed for the catalyst without cobalt (15, 21) and also for a NiO-MgO solid solution (22, 23), except for a small hump between 400° and 650°C (Fig. 4.3.1). The hump is more pronounced for the catalyst with higher Co/Ni ratios and it is shifted towards the lower temperature side with increasing the Co/Ni ratio. The peak maximum temperature for all the TPR curves is 900°C. However, this is not a true peak maximum temperature as the maximum temperature chosen for the TPR itself is 900°C. Hence, true maximum temperature is expected to be above 900°C.

TABLE 4.3.1 Surface Area and Degree of Reduction (in the TPR) of the Co_xNi_{1-x}O/MgO/SA-5205^a (x = 0.0-0.5) the Catalysts.

X	Co/Ni Mol ratio	Surface area (m ² g ⁻¹)	Degree of reduction (%)
0.0	0.0	2.0	34.5
0.05	0.05	1.9	49.7
0.15	0.17	1.6	61.7
0.29	0.4	1.3	65.1
0.50	1.0	1.1	72.5

^a Surface area of the support (SA-5205) <0.01 m² g⁻¹

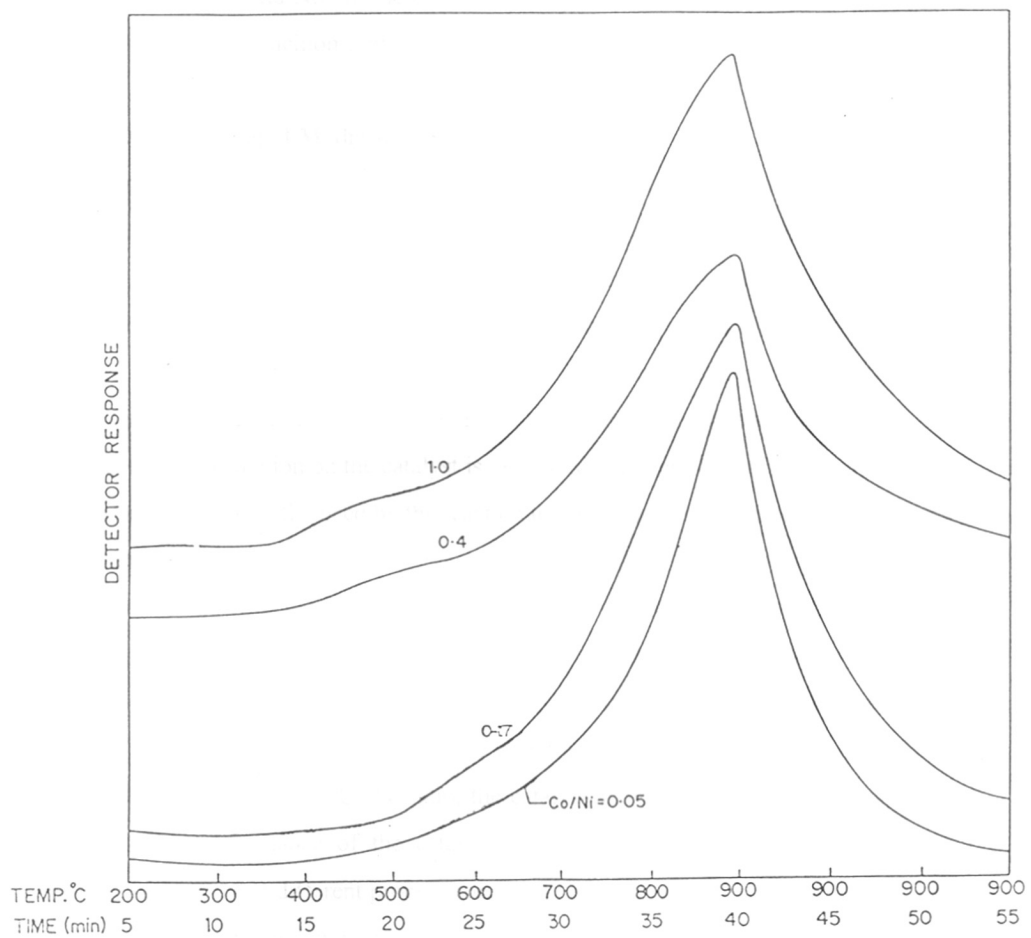


Fig. 4.3.1.:TPR of the catalysts with different Co/Ni ratios.

The degree of reduction of $\text{Co}_x\text{Ni}_{1-x}\text{O}$ from the catalyst is increased with increasing its Co/Ni ratio (Table 4.3.1). The degree of reduction was estimated from the knowledge of the concentration of CoO and NiO in the catalyst and the amount of H_2 consumed in the TPR, and assuming the reaction stoichiometry (CoO or $\text{NiO} + \text{H}_2 \rightarrow \text{Co}^0$ or $\text{Ni}^0 + \text{H}_2\text{O}$).

4.3.2.2. CO_2 Reforming of Methane to Syngas

In order to find the influence of Co/Ni ratio on the extent of filamental carbon formation on the catalyst, particularly in the CO_2 reforming of methane at different temperatures, a pressure drop across the catalyst bed after a reaction period of 1.0 h was measured. Results showing the influence of Co/Ni ratio on the pressure drop across the catalyst bed due to filamental carbon formation in the CO_2 reforming at different temperatures ($700^\circ\text{-}900^\circ\text{C}$) are presented in Fig.4.3.2. At all the temperatures the pressure drop and consequently the extent of filamental carbon formation on the catalyst is decreased exponentially with increasing the Co/Ni ratio. It is also strongly influenced by the reaction temperature; it is increased with increasing the temperature.

Results showing the influence of Co/Ni ratio of the catalyst on the conversion, H_2 selectivity, and H_2/CO product ratio in the CO_2 reforming of methane to syngas for a low contact time (high space velocity) are presented in Fig. 4.3.3. At all the temperatures, the conversion, selectivity and H_2/CO ratio passed through a maximum at the Co/Ni ratio of about 0.17. This indicates that at this optimum Co/Ni ratio, the catalyst shows the best performance in the CO_2 reforming. The performance of the catalyst with optimum Co/Ni ratio (0.17) in the CO_2 reforming of methane at different process conditions is presented in Fig. 4.3.4. Figure 4 3.4 also shows the influence of temperature, space velocity and CH_4/CO_2 feed ratio on the conversion of both methane and CO_2 , H_2 selectivity and H_2/CO product ratio in the process.

Following general observations can be made from the results (Figs.4.3.3 and 4.3.4):

- The conversion of CO_2 is higher than that of CH_4 .
- The H_2 selectivity is less than 100%.
- The H_2/CO ratio is less than 1.0.

These observations indicate that, along with the CO_2 reforming of methane,



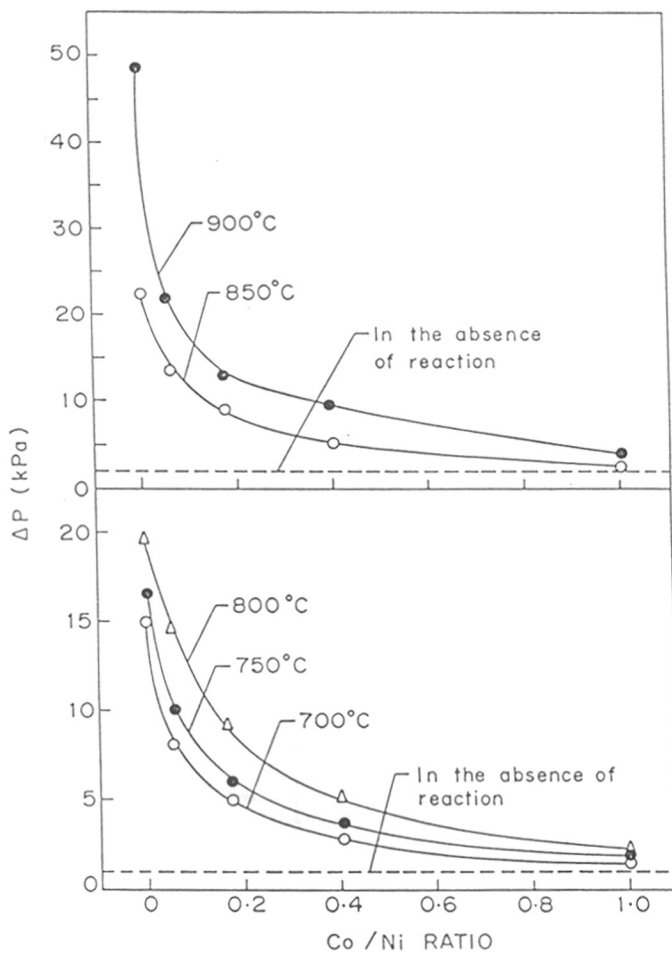


Fig. 4.3.2 :Influence of Co/Ni ratio in the catalyst on the pressure drop across the catalyst bed in the CO_2 reforming of methane over the catalysts at different temperatures (CO_2/CH_4 feed ratio = 1.0 and $\text{GHSV} = 3.9 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$).

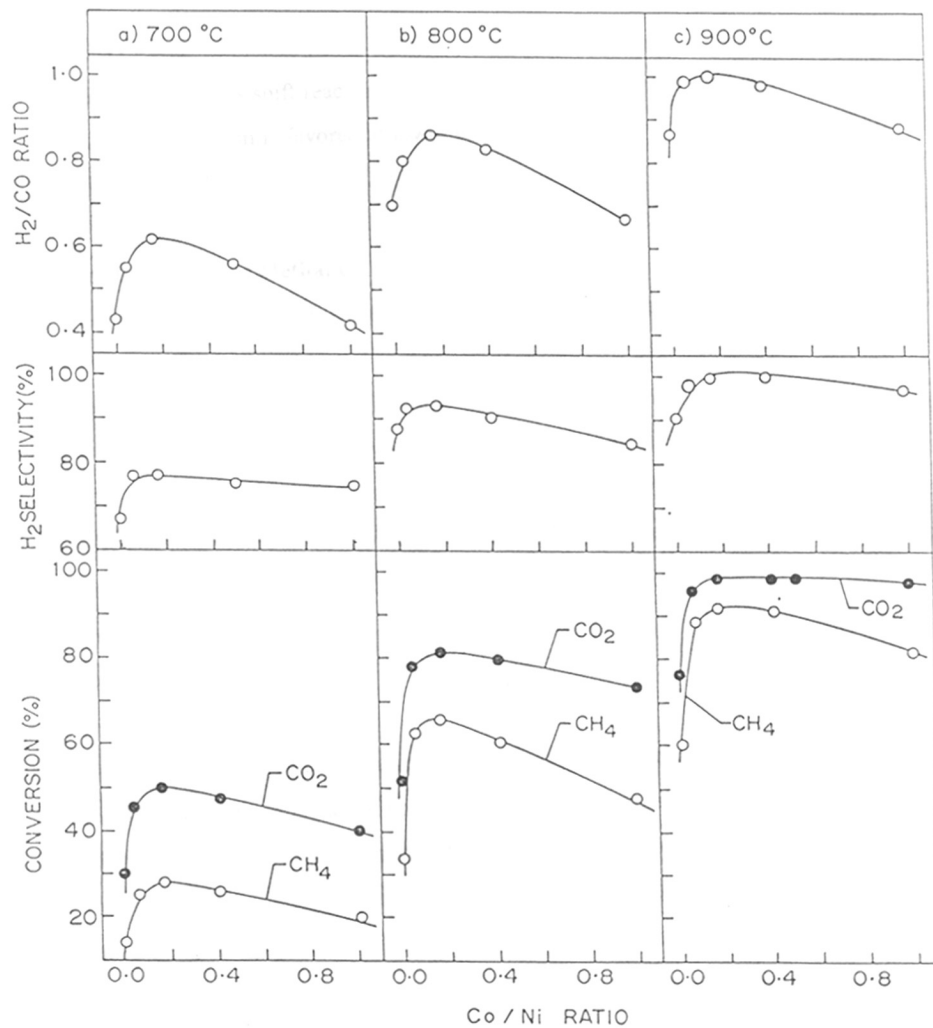


Fig. 4.3.3.: Influence of Co/Ni ratio in the catalyst on its performance in the CO₂ reforming of methane at different temperatures (CO₂/CH₄ feed ratio = 1.0 and GHSV = 3.9 x 10⁴ cm³ g⁻¹ h⁻¹).

a side reaction,



which is a reverse water gas shift reaction, occurs simultaneously, depending upon the process conditions. This side reaction is favored at lower temperature, higher space velocity and higher CO_2/CH_4 ratio (Fig. 4.3.4).

4.3.2.3. Steam Reforming of Methane

Figure 4.3.5 shows the influence of Co/Ni ratio in the catalyst on the conversion of methane and water, CO selectivity and H_2/CO product ratio in the steam reforming of methane at two different temperatures. With the increase in the Co/Ni ratio, the conversion of methane and water is decreased, the CO selectivity is also decreased and the H_2/CO ratio in the product is increased. The influence is particularly stronger at the lower temperature. The decrease in the CO selectivity and/or increase in the H_2/CO ratio with increasing the Ni/Co ratio indicates that along with steam reforming of methane,



the water-gas reaction,



occurs to an increasing extent with increasing the Co/Ni ratio of the catalyst.

Results showing the influence of process variables on the conversion, CO selectivity and H_2/CO product ratio in the steam reforming of methane over the catalysts with Co/Ni ratio of 0.17 are presented in Fig. 4.3.6. It is evident from the results that the side reaction is more predominant at the lower temperature, higher space velocity and higher $\text{H}_2\text{O}/\text{CH}_4$ feed ratio.

In the steam reforming of methane over all the catalysts, the pressure drop across the catalyst bed was negligibly small, indicating little or no filamental carbon formation during the process.

4.3.2.4. Simultaneous CO_2 and Steam Reforming of Methane

Figure 4.3.7 shows the influence of Co/Ni ratio in the catalyst the performance (conversion of methane, CO_2 and water and H_2/CO product ratio) in the simultaneous CO_2 and steam reforming of methane (reactions 1 and 3). The catalyst performance is strongly influenced

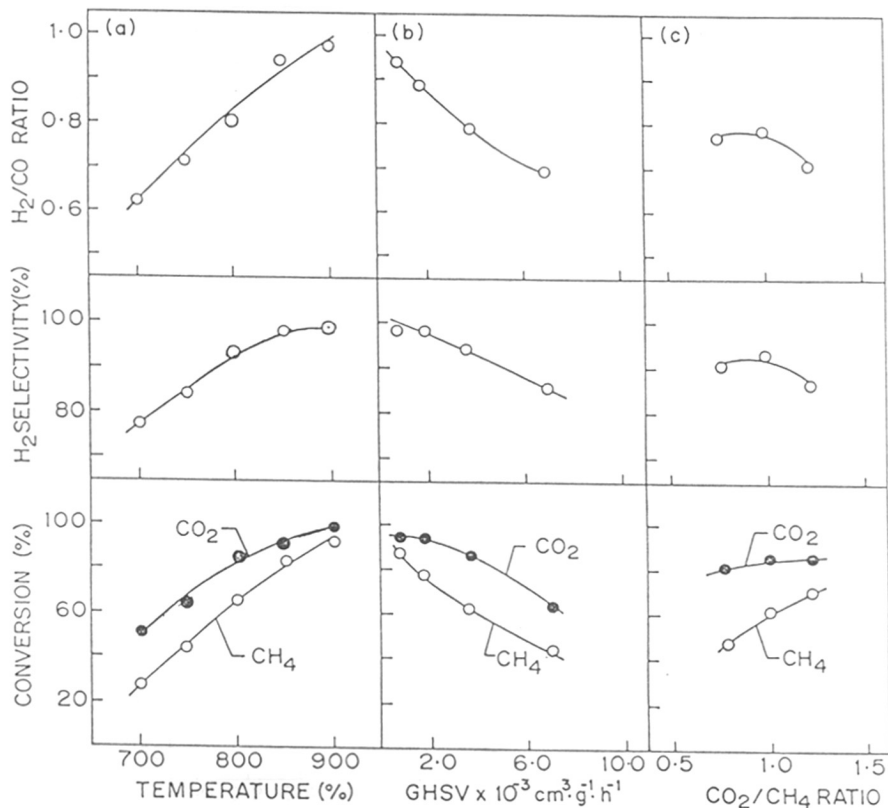


Fig. 4.3.4.:Influence of a) reaction temperature ($\text{CH}_2/\text{CH}_4 = 1.0$ and $\text{GHSV} = 3.9 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$) b) space velocity (at 800°C and $\text{CO}_2/\text{CH}_4 = 1.0$) and c) CO_2/CH_4 ratio (at 800°C and $\text{GHSV} = 3.9 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$) on the conversion, CO selectivity and H_2/CO product ratio in the steam reforming of methane over the catalyst with Co/Ni ratio of 0.17.

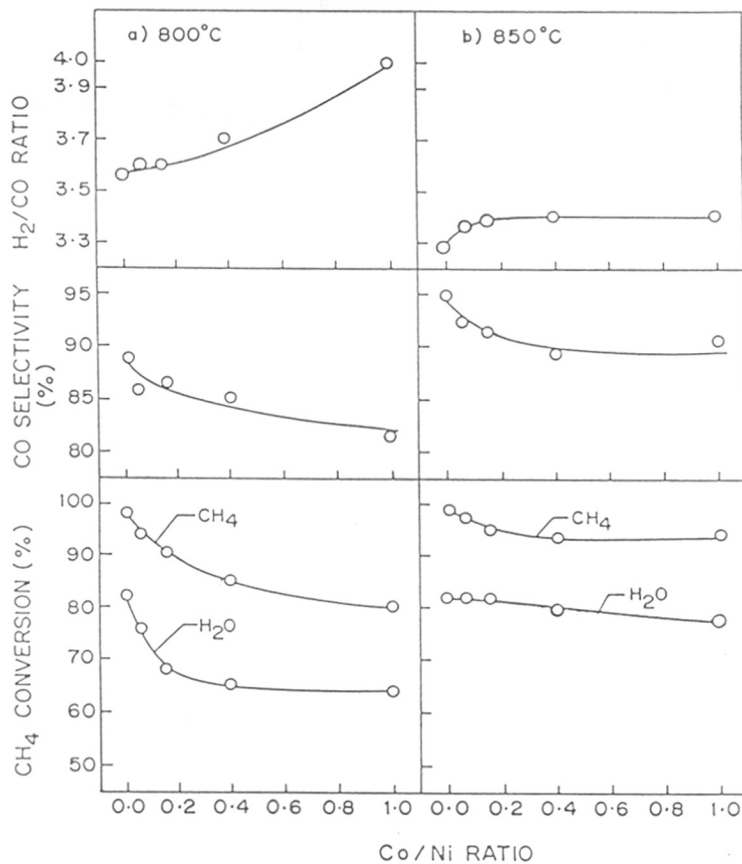


Fig. 4.3.5.:Influence of Co/Ni ratio in the catalyst on its performance in the steam reforming of methane at 800° and 850°C (H_2O/CH_4 feed ratio = 1.54 and GHSV = $2.3 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$).

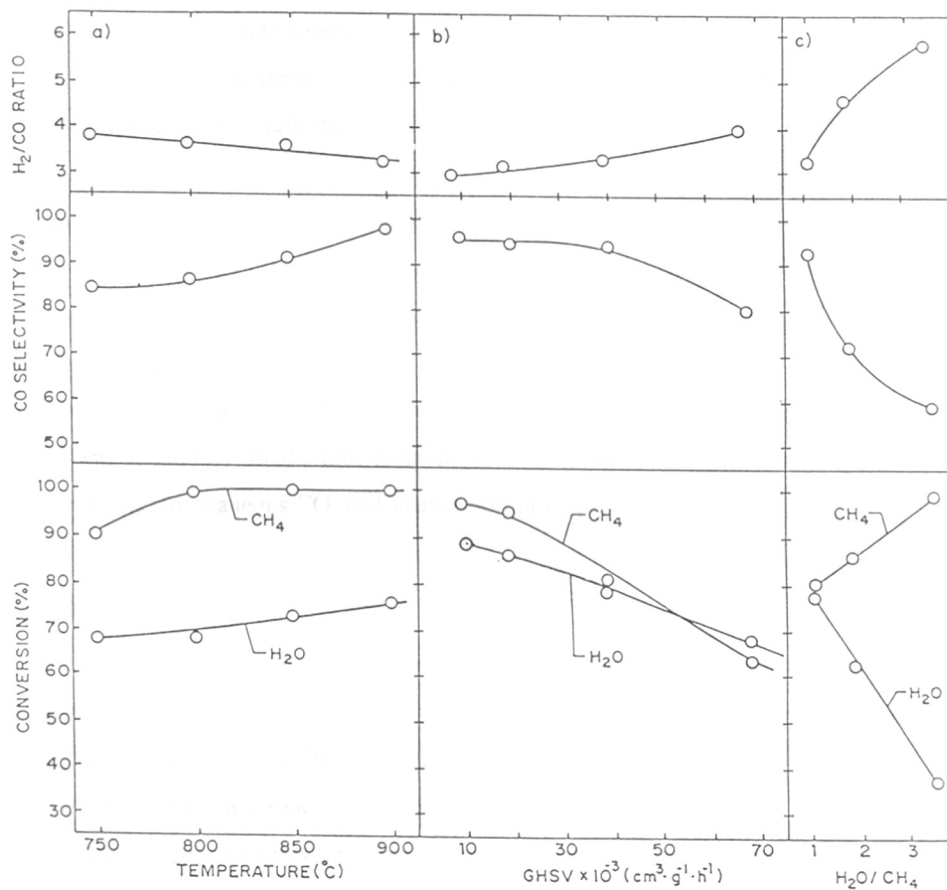


Fig. 4.3.6: Influence of a) reaction temperature ($\text{H}_2\text{O}/\text{CH}_4 = 1.56$ and $\text{GHSV} = 2.3 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$) b) space velocity (at 800°C and $\text{H}_2\text{O}/\text{CH}_4 = 1.15$) and c) $\text{H}_2\text{O}/\text{CH}_4$ ratio (at 800°C and $\text{GHSV} = 4.5 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$) on the conversion, CO selectivity and H_2/CO product ratio in the steam reforming of methane over the catalyst with Co/Ni ratio of 0.17.

by the Co/Ni ratio, similar to that was observed for the CO₂ reforming of methane. In this case also, the catalyst shows highest activity when its Co/Ni ratio is 0.17 the conversion of all the reactants is passed through a maximum for the catalyst with (Co/Ni ratio = 0.17). The H₂/CO ratio is however passed through a minimum at this Co/Ni ratio (Fig. 4.3.7).

Results showing the performance of the catalyst with its optimum Co/Ni ratio in the simultaneous CO₂ and steam reforming process at different process conditions are presented in Figs. 4.3.8 and 4.3.9.

Results in Fig. 4.3.8 show a strong influence of space velocity on the conversion of all the reactants but almost no effect on the H₂/CO ratio. The H₂/CO ratio is, however, decreased markedly with increasing the CO₂/H₂O feed ratio for a constant (CO₂ + H₂O)/CH₄ feed ratio (Fig. 4.3.9).

The pressure drop across the catalyst bed for all the catalysts at the different process conditions was negligibly small, indicating little or no filamental carbon formation on the catalyst during the simultaneous CO₂ and steam reforming process.

4.3.3.DISCUSSION

The above results reveal that the surface properties, filamental carbon formation in the CO₂ reforming of methane and catalytic activity in the CO₂ and/or steam reforming of methane are strongly influenced by increasing the Co/Ni ratio of the catalyst.

The decrease in the surface area with increasing the Co/Ni ratio (Table 4.3.1) indicates that the addition of cobalt causes sintering or crystal growth of the catalyst. Since the surface area of the support is very low (0.01 m² g⁻¹), the observed surface area of the catalyst is mainly because of the active catalytic components (i.e. oxides of nickel and Co and MgO) deposited on the support.

The dependence of the trend of the TPR curves (Fig. 4.3.1) and degree of catalyst reduction (Table 4.3.1) on the Co/Ni ratio shows that the rate of catalyst reduction is enhanced because of the addition of cobalt to the catalyst. The observed hump at low temperature may be due to a faster reduction of that of cobalt oxide which has not formed a solid solution in the MgO. Both NiO and CoO can form a complete solid solution in MgO (22). However, since the ionic radius of Co²⁺ (0.72°A) is larger than that of Ni²⁺ (0.69°A) (the ionic radius of Mg²⁺ is

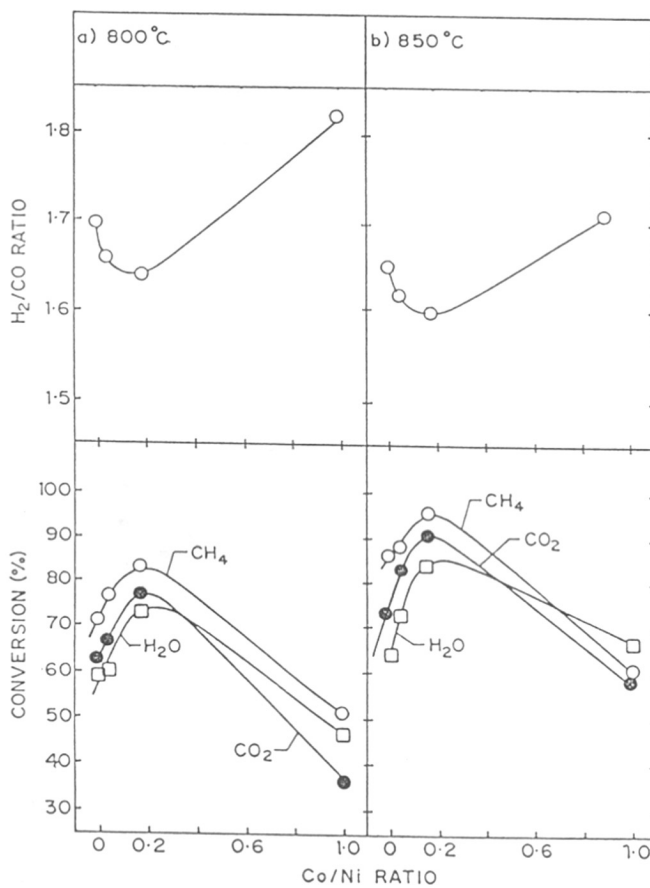


Fig. 4.3.7.:Influence of Co/Ni ratio in the catalyst on its performance in the simultaneous CO_2 and steam reforming of methane at 800° and 850°C(CO_2/CH_4 feed ratio = 0.55, H_2O/CH_4 feed ratio = 0.57 and $GHSV = 5.1 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$).

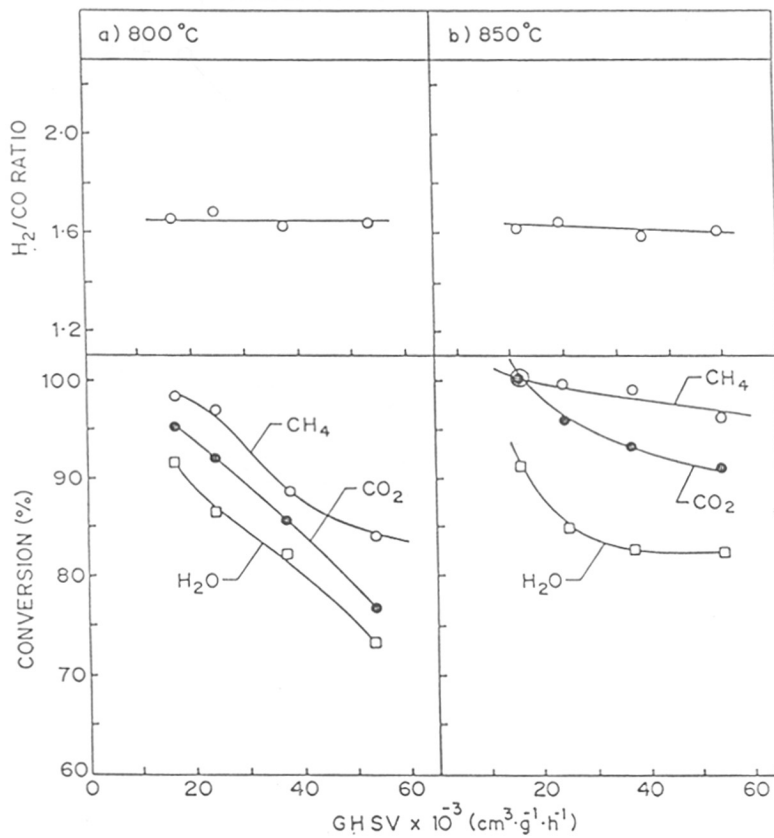


Fig. 4.3.8: Influence of GHSV on the conversion and H₂/CO product ratio in the simultaneous steam and CO₂ reforming of methane over the catalyst with Co/Ni ratio of 0.17 at 800° and 850°C (CO₂/CH₄ and H₂O/CH₄ feed ratios = 0.57 and 0.57, respectively).

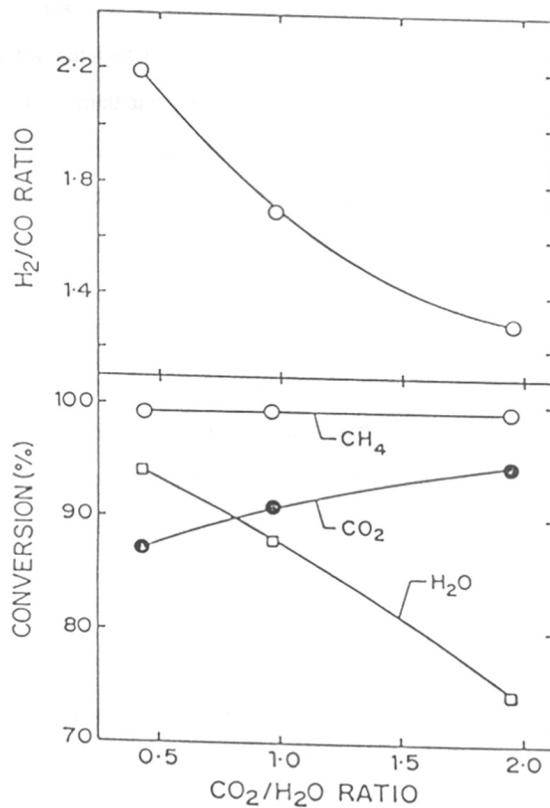


Fig. 4.3.9.: Influence of $\text{CO}_2/\text{H}_2\text{O}$ feed ratio on the conversion and H_2/CO product ratio in the simultaneous CO_2 and steam reforming of methane over the catalyst with Co/Ni ratio of 0.17 at 850°C ($2.3 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$). [$(\text{CO}_2 + \text{H}_2\text{O})/\text{CH}_4$ feed ratio = 1.2 and $\text{GHSV} = 2.3 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$].

0.66°A), the formation of solid solution of CoO in MgO is difficult as compared to that of NiO in MgO.

The higher pressure drop across the reactor for the catalyst containing nickel alone (i.e. without cobalt) is resulted from the filamental (whisker) carbon on the catalyst (24,25) leading to plugging of the catalyst bed. The carbon formation can be due to the Boudouard reaction ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$), methane decomposition ($\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$) and heterogeneous water gas reaction ($\text{CO} + \text{H}_2 \rightarrow \text{C} + \text{H}_2\text{O}$), occurring simultaneously. The observed large decrease in the filamental carbon formation with increasing the Co/Ni ratio of the catalyst (Fig. 4.3.2) is attributed mostly to its reduced activity for the above carbon forming reactions. Such beneficial effect was also observed earlier in case of the oxidative conversion of methane to syngas over Ni and Co containing Yb_2O_3 , ZrO_2 and ThO_2 catalysts (20).

The nickel and cobalt oxides in the catalyst are reduced to their metallic form in the initial short reaction period (< 30 min.), first by methane and then by hydrogen produced in the reforming of methane over the partially reduced catalyst.

In the steam reforming of methane, both the activity and selectivity of the catalyst are decreased with increasing the Co/Ni ratio (Fig. 4.3.5). However, in the CO_2 reforming and simultaneous CO_2 and steam reforming processes, the catalyst shows best performance at the optimum Co/Ni ratio (0.17) (Figs. 4.3.3 and 4.3.7). Thus, the addition of cobalt to the catalyst at the optimum concentration has a beneficial effect in these latter two processes not only for reducing drastically the filamental coke formation but also or enhancing the catalytic activity and also increasing selectivity, particularly for the CO_2 reforming reaction. It may be noted that, in the simultaneous CO_2 and steam reforming processes, there is no formation of any side product and hence, as long as the conversion of both CO_2 and water is positive, the selectivity for H_2 and CO in the conversion of methane to syngas is always 100%.

The results reveal that the catalyst with optimum Co/Ni ratio of 0.17 is a highly promising catalyst for the CO_2 reforming and simultaneous CO_2 and steam reforming processes showing high activity for methane -to-CO and H_2 conversion at low contact time or high space velocity with less carbon formation on the catalyst.

Among the steam and/or CO₂ reforming processes, the simultaneous CO₂ and steam reforming of methane is a process of great practical importance because of the following interesting features

- Unlike the CO₂ reforming process, the carbon formation on the catalyst is much less and the H₂ selectivity (based on methane conversion) is 100%.
- Unlike the steam reforming process, there is no formation of undesired product such as CO₂ (which has high green house effect) and hence, the CO selectivity (based on methane conversion) is 100%.
- The H₂/CO product ratio can be varied between 1.0 and 3.0 by manipulating the CO₂/H₂O feed ratio.

4.3.4.CONCLUSIONS

From this investigation, following important conclusions have been drawn.

- 1) The surface and reduction properties, filamental carbon formation in the CO₂ reforming of methane, and methane-to-syngas conversion activity (in the steam and/or CO₂ reforming of methane) over the Co_xNi_{1-x}O/MgO/SA-5205 catalyst (x = 0-0.5) are strongly influenced by the Co/Ni ratio in the catalyst.
- 2) Because of the increase in the Co/Ni ratio, the surface area of the catalyst is decreased, but its degree of reduction is increased.
- 3) The presence of cobalt in the catalyst has a beneficial effect on the formation of filamental carbon; the carbon formation is drastically reduced with increasing the Co/Ni ratio in the catalyst. (It is reduced in the CO₂ reforming of methane.
- 4) The presence of cobalt in the catalyst at an optimum Co/Ni ratio (0.17) has also a beneficial effect on the methane-to-H₂ and CO conversion activity in the CO₂ reforming and simultaneous CO₂ and steam reforming processes. However, in the steam reforming process, it has an adverse effect on the both activity and selectivity of the catalyst.

- 5) The catalyst with the optimum Co/Ni ratio is highly promising catalyst for the conversion of methane to CO and H₂, particularly by the simultaneous CO₂ and steam reforming process.

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CHAPTER-4.4

OXY-CO₂ REFORMING, OXY-STEAM REFORMING AND OXY-CO₂ AND STEAM REFORMING OF METHANE OVER Co_xNi_{1-x}O SUPPORTED ON MACROPOROUS SILICA-ALUMINA PRECOATED WITH MgO

4.4.1 EARLIER LITERATURE AND OBJECTIVES OF THE PRESENT WORK

Catalytic oxidative conversion of methane to syngas (a mixture of CO and H₂), at a very low contact time (1-2 ms at the reaction conditions) (1-12), is a process of great practical importance. This process, unlike the conventional steam reforming process, is mildly exothermic and hence, not at all energy intensive and moreover, it can provide syngas with H₂/CO product ratio (about 2.0), suitable for the methanol and/or Fischer-Tropsch synthesis processes without any downstream processing. A number of nickel, cobalt and/or noble metal containing catalysts [viz., NiO-MgO (1), NiO-CaO (2), CoO-MgO (13), CoO or NiO-rare earth oxides (3, 6), LaNiO₃ (11), Ni/Al₂O₃ with or without Pt (7), supported noble metals (4,5,8,9), NiO-CoO-Yb₂O₃ or -ZrO₂ or -ThO₂ (14), NiO supported on commercial low surface area catalyst carriers precoated with alkaline and rare earth oxides (10,12)], showing high activity and selectivity at a very low contact time (1-2 ms), have been reported for this process.

In all the above studies, the amount of catalyst used was very small (≤ 20 mg) and hence, there was no serious problem for the removal of heat from the reactor. But, when large amount of catalyst (1.0 gm) was used, it was extremely difficult to control the reaction because of the limitations imposed by heat removal from the reactor (15). The oxidative methane-to-syngas conversion process is highly hazardous and difficult to practice, in spite of the fact that the partial oxidation of methane to CO and H₂ is mildly exothermic ($\Delta H_r = -5.4$ kcal mol⁻¹) and the selectivity is high (95%). This is because of the fact that a very low contact time coupled with high conversion ($\geq 90\%$) results in production of a large amount of heat in a very small catalyst zone, the removal of which is very difficult. Moreover, a small decrease in the selectivity by some reason, can result in a drastic increase in the heat produced due to the combustion of methane to CO₂ and water, making the process control still more difficult and/or leading to process run-away. In order to overcome this limitation, efforts have been made to carry out the

exothermic oxidative methane-to-syngas conversion simultaneously with the endothermic steam reforming of methane (16, 17), or CO₂ reforming of methane (17-19) or with both (11, 17, 20, 21); the exothermic and endothermic reactions could be coupled successfully, making the process energy efficient and non-hazardous or safer.

In the earlier studies (12, 17), NiO supported on low surface area macroporous silica-alumina catalyst carrier precoated with MgO showed high activity and selectivity in the oxidative conversion of methane to syngas with or without simultaneous steam and/or CO₂ reforming over the same catalyst. An addition of cobalt to nickel containing Yb₂O₃, ZrO₂ and ThO₂ catalysts caused a drastic reduction in the filamental carbon formation on them but a small decrease in the selectivity for both CO and H₂ in the oxidative conversion of methane to syngas. An addition of cobalt to supported nickel catalyst (NiO/MgO/SA-5205) resulted in a drastic reduction in the carbon formation in the CO₂ reforming of methane to syngas (Chapter 4.3) It is, therefore, interesting to study the effect of cobalt addition to the above supported nickel catalyst on its performance (activity and selectivity) in the oxy-CO₂ reforming, oxy-steam reforming and oxy-CO₂ and steam reforming reactions of methane for its conversion to syngas at low contact time for developing a better catalyst for these processes. The present work was undertaken for this purpose.

4.4.2.RESULTS

4.4.2.1.Oxy-CO₂ Reforming of Methane

Results showing the influence of Co/Ni ratio on the conversion, selectivity and H₂/CO product ratio in the oxy-CO₂ reforming of methane to CO and H₂ over the catalyst at three different process conditions are presented in Fig. 4.4.1. With the increase of Co/Ni ratio of the catalyst, the conversion, H₂ selectivity and H₂/CO product ratio are influenced as follows :

- The conversion of both CH₄ and CO₂ is passed through a maximum at the Co/Ni ratio of 0.17.
- The H₂ selectivity is also passed through a maximum at the Co/Ni ratio of 0.17; the CO selectivity is, however, remained constant (100%).
- The H₂/CO ratio is, however, not changed significantly.

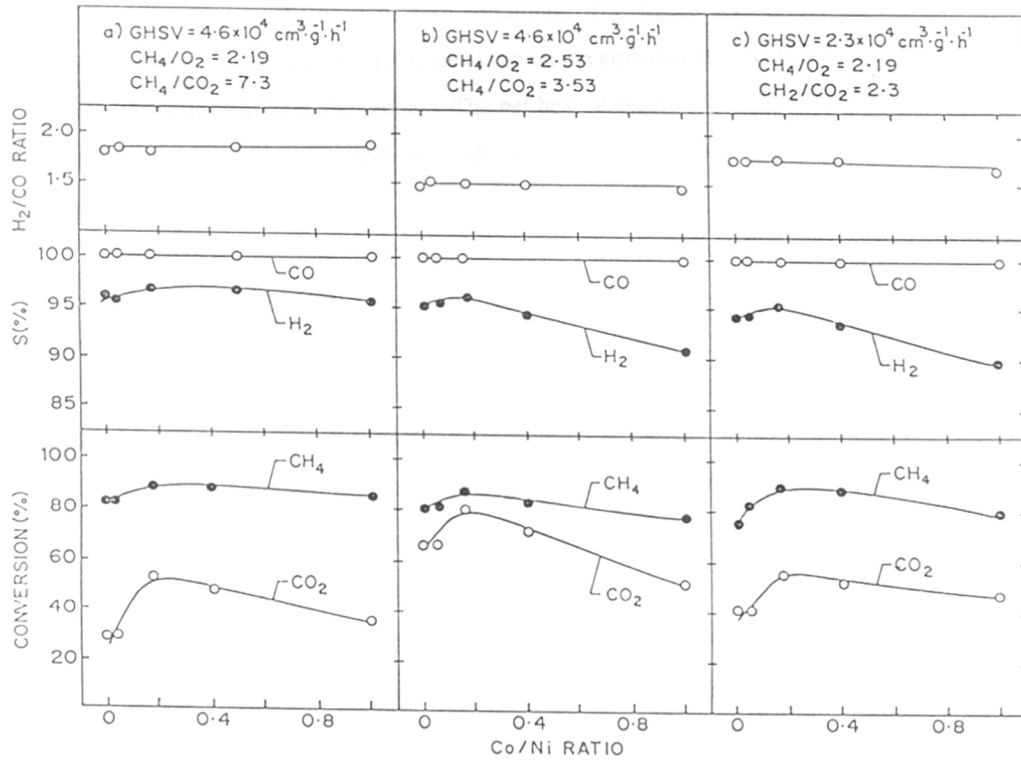


Fig. 4.4.1.: Effect of Co/Ni ratio of the catalyst on its performance in the oxy- CO_2 reforming of methane at 800°C .

These observations suggest that the catalyst with Co/Ni ratio of 0.17 shows optimum performance in the oxy-CO₂ reforming process.

Figure 4.4.2 shows the performance of the catalyst with the optimum of Co/Ni ratio (0.17) in the process at different process conditions. The figure also shows the influence of temperature, space velocity and CH₄/O₂ feed ratio on the conversion, selectivity, H₂/CO ratio and net heat of reaction (ΔHr) in the process. The net heat of reaction was estimated by subtracting the heat of formation (at the reaction conditions) of the reactants from that of the products formed in the process.

Results in Fig. 4.4.2 show that the influence of space velocity (i.e. contact time) is small but that of the temperature and CH₄/O₂ ratio is appreciable. When the temperature is increased, the conversion of both CH₄ and CO₂, H₂ selectivity and net heat of reaction (ΔHr) (or process endothermicity) are increased but a CO selectivity (which is 100%) and H₂/CO ratio are remained constant. However, when the CH₄/O₂ ratio is increased,

- the conversion of methane is not changed significantly but that of CO₂ is increased markedly,
- the H₂ selectivity is also increased but the increase is small,
- the H₂/CO ratio is decreased appreciably, and
- the heat of reaction (ΔHr) or process endothermicity is increased markedly.

The observed high conversion of all the reactants (CH₄, O₂ and CO₂) and the appreciable increase in the process endothermicity with increasing the temperature or CH₄/O₂ feed ratio (Figs. 4.4.1 and 4.4 2) indicate an occurrence of the exothermic oxidative conversion of methane,



along with endothermic CO₂ reforming of methane,



over the same catalyst in the oxy-CO₂ reforming process.

Unlike the CO₂ reforming of methane over the catalysts (22), no significant increase in the pressure drop across the catalyst bed due to the formation of filamental carbon during the oxy-CO₂ reforming of methane (for a period of 1h) was observed.

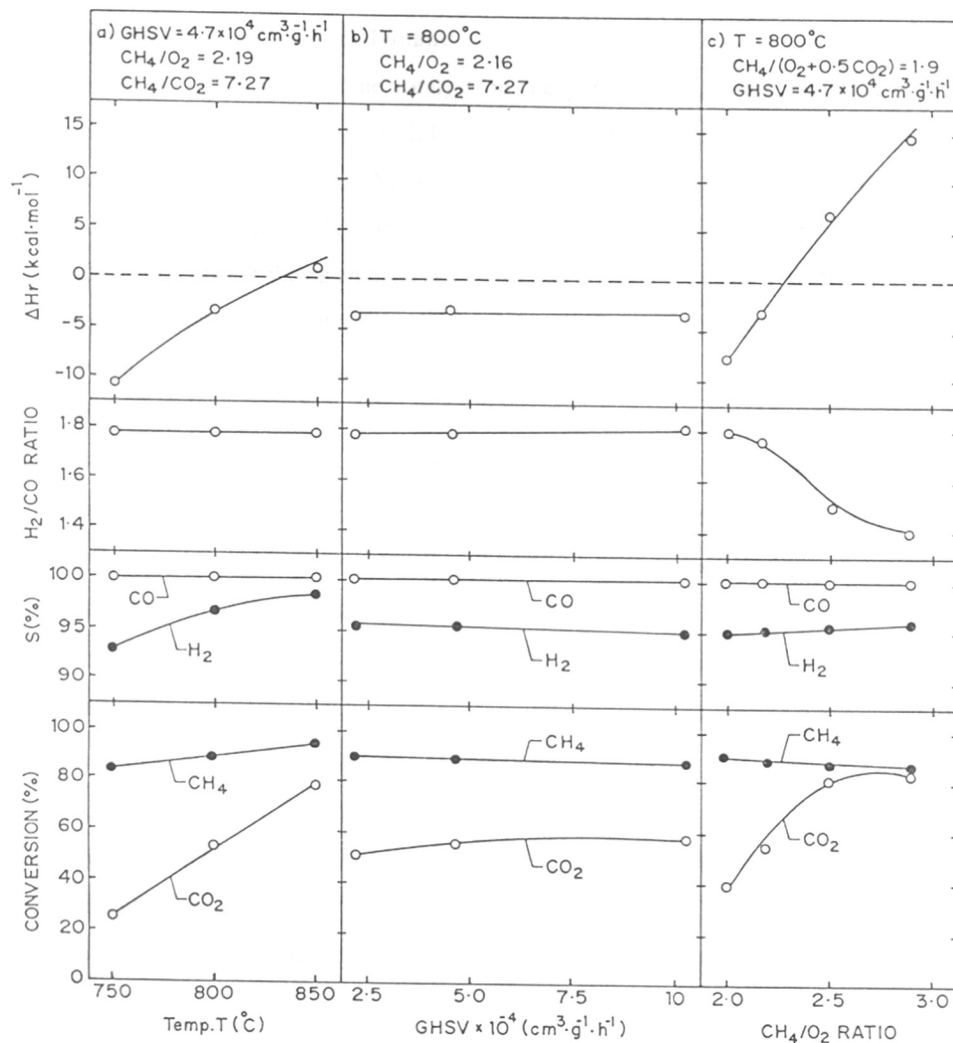


Fig. 4.4.2.:Effect of a) reaction temperature b) space velocity and c) CH₄/O₂ feed ratio on the conversion, selectivity, H₂/CO product ratio and net heat of reaction (ΔH_r) in the oxy-CO₂ reforming of methane over the catalyst with Co/Ni ratio of 0.17. *

4.4.2.2. Oxy-Steam Reforming of Methane

Effect of Co/Ni ratio of the catalyst on the performance in the oxy-CO₂ reforming process at different temperatures and CH₄/O₂ and CH₄/H₂O feed ratios is shown in Figs 4.4.3 and 4.4.4. The results reveal that the Co/Ni ratio has a small effect on the conversion, selectivity and H₂/CO ratio. The effect, particularly on the CO selectivity depends upon the process conditions. Nevertheless, the catalyst shows an optimum performance in this process when its Co/Ni ratio is 0.17. The -ve conversion of water (Fig. 4.4.3a) indicates that there is a net formation of water in the process at the low CH₄/O₂ feed ratio (or at the high CH₄/H₂O).

Results showing the influence of CH₄/O₂ ratio [at constant CH₄/(O₂ + 0.5H₂O) ratio of 1.82] at different temperatures (800° and 850°C) on the conversion, selectivity and net heat of reaction (ΔHr) in the oxy-steam reforming process over the catalyst with the optimum Co/Ni ratio (0.17) are presented in Fig 4.4.5. When the CH₄/O₂ ratio is increased (or concentration of water relative to that of O₂ is increased) at both the temperatures,

- there is a small but continuous decrease in the methane conversion but an appreciable increase in the water conversion,
- there is a little or no influence on the CO selectivity,
- the H₂/CO product ratio is increased appreciably, and
- the process endothermicity is increased markedly, converting the mildly exothermic process (at the higher CH₄/O₂ ratios).

These results indicate that, in the oxy-steam reforming process, the steam reforming of methane,



occurs along with the oxidative conversion of methane (reaction 1).

4.4.2.3. Simultaneous Oxy-CO₂ and Steam Reforming of Methane

In this process, a mixture of methane, oxygen, CO₂ and steam is passed over the catalyst at desired process conditions.

Results showing the influence of Co/Ni ratio of the catalyst on the performance in the process at three different process conditions are presented in Fig. 4.4.6. The results show a little or no effect of the Co/Ni ratio of the catalyst on the conversion of methane and H₂/CO product

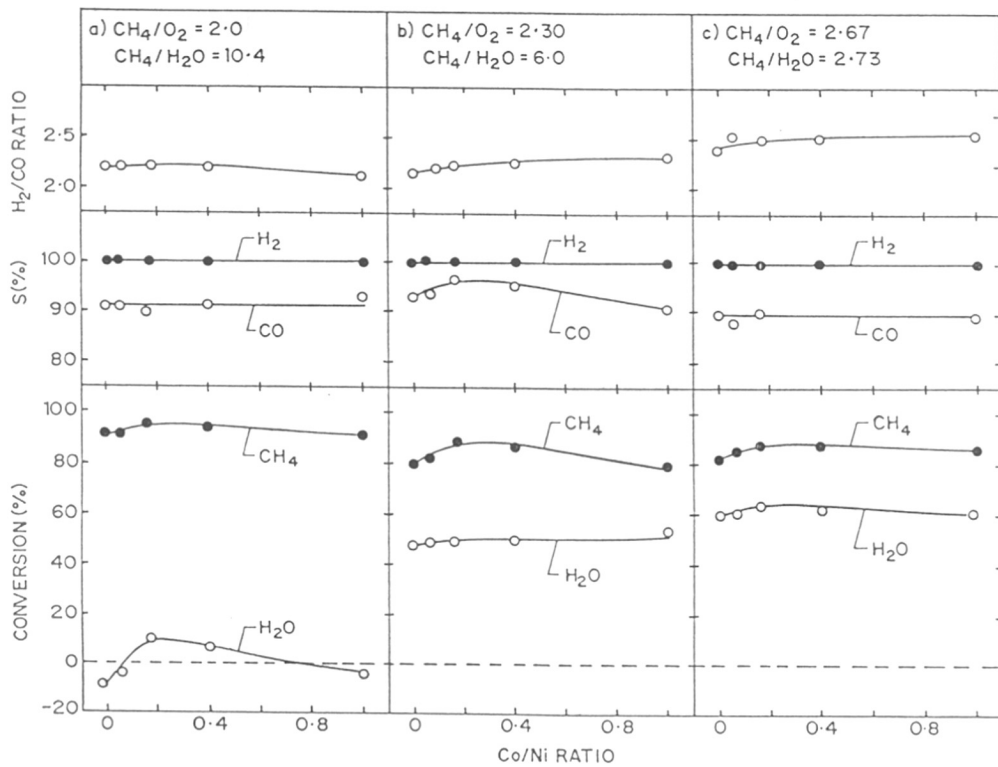


Fig. 4.4.3.:Effect of Co/Ni ratio of the catalyst on its performance in the oxy-steam reforming of methane at 800°C (GHSV = $4.7 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$).

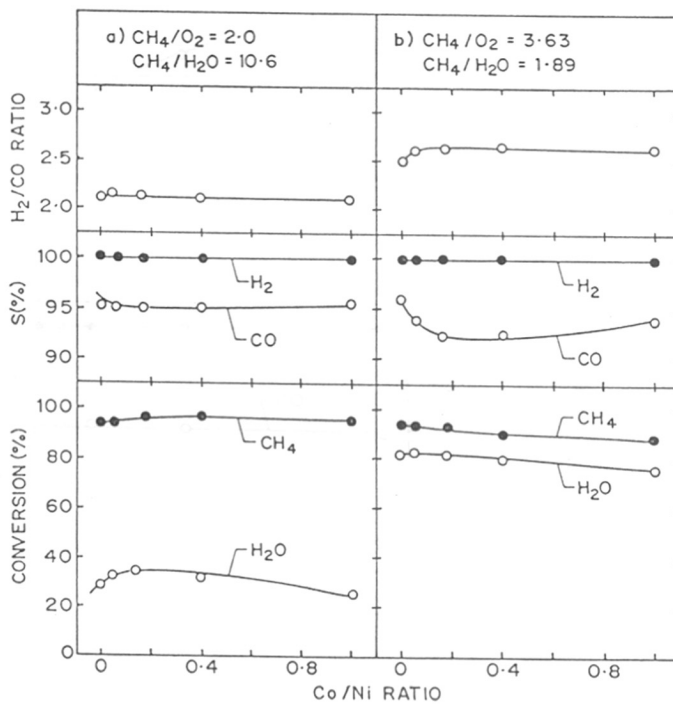


Fig. 4.4.4.:Effect of Co/Ni ratio of the catalyst on its performance in the oxy-steam reforming of methane at 850°C (GHSV = $4.7 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$).

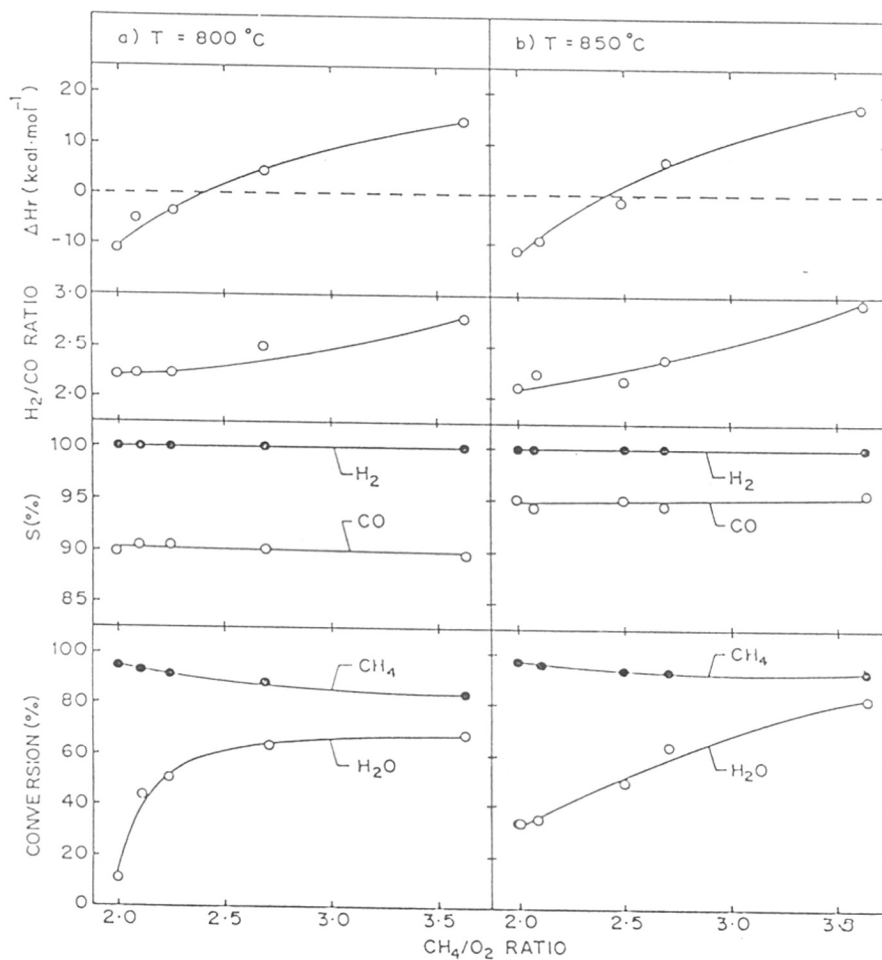


Fig. 4.4.5.:Effect of a) reaction temperature b) space velocity and c) CH_4/O_2 feed ratio on the conversion, selectivity, H_2/CO product ratio and net heat of reaction (ΔH_r) in the oxy-steam-reforming of methane over the catalyst with Co/Ni ratio of 0.17 at 800° and 850°C [$\text{CH}_4/(\text{O}_2 + 0.5\text{H}_2\text{O}) = 1.82$, GHSV = $4.7 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$].

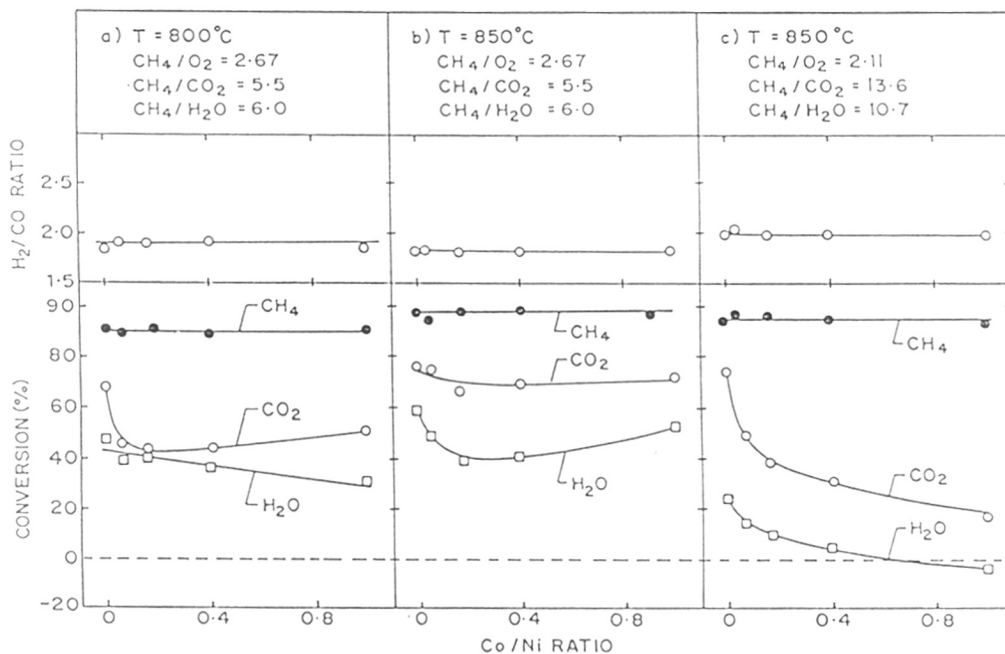


Fig. 4.4.6.: Effect of Co/Ni ratio of the catalyst on its performance in the simultaneous oxy-CO₂ and steam reforming of methane at different temperatures and CH₄/O₂, CH₄/CO₂, CH₄/H₂O feed ratios [CH₄/(O₂ + 0.5H₂O) = 1.8, GHSV = 4.6 × 10⁴ cm³ g⁻¹ h⁻¹].

ratio but a strong effect on the conversion of CO_2 and water, depending upon the process conditions.

The performance of the catalyst with Co/Ni ratio of 0.17 and 1.0, showing the influence of CH_4/O_2 feed ratio [while keeping the $\text{CH}_4/(\text{O}_2 + 0.5\text{CO}_2 + 0.5\text{H}_2\text{O})$ and $\text{CO}_2/\text{H}_2\text{O}$ ratios constant (which are 1.8 and 1.0, respectively)], on the conversion, H_2/CO product ratio and the net heat of reaction (ΔHr) at two different temperatures is presented in Figs.4.4.7 and 4.4.8. The trend for the influence of CH_4/O_2 feed ratio for both the catalysts is similar. When the CH_4/O_2 ratio is increased, its influence on the process is as follows.

- There is a small but significant decrease in the methane conversion but an appreciable increase in the conversion of CO_2 and H_2O .
- The H_2/CO ratio is decreased but the decrease is small.
- The process endothermicity is increased markedly, thus converting the exothermic process (at the lower CH_4/O_2 ratios) into the endothermic one (at the higher CH_4/O_2 ratios).

Results in Table 4.4.1 show a strong influence of the $\text{CO}_2/\text{H}_2\text{O}$ feed ratio [when the CH_4/O_2 and $\text{CH}_4/(\text{O}_2 + \text{H}_2\text{O})$ feed ratios are kept constant on the H_2/CO product ratio in the process over the catalyst with Co/Ni ratio of 0.17 and 1.0. The H_2/CO ratio is decreased with increasing the $\text{CO}_2/\text{H}_2\text{O}$ ratio. However, the influence of the $\text{CO}_2/\text{H}_2\text{O}$ ratio on the methane conversion is negligibly small.

In the oxy- CO_2 and steam reforming process, methane is converted into CO and H_2 not only by its oxidative conversion (reaction 1) but also by its CO_2 reforming (reaction 2) and steam reforming (reaction 3). Hence, there is no formation of any side product, as long as the conversion of both steam and CO_2 is greater than or equal to zero.

4.4.3.DISCUSSION

4.4.3.1.Coupling of Oxidative Conversion with CO_2 and/or Steam Reforming of Methane

In all the three methane-to-syngas conversion processes (Oxy- CO_2 reforming, Oxy-steam reforming, and Oxy- CO_2 and steam reforming), the conversion of O_2 was above 98% at all the process conditions. With the increase of the CH_4/O_2 feed ratio, there is a small decrease in the conversion of methane but a large increase in the conversion of CO_2 and/or steam; high CO_2 and/or steam conversion is observed only for the higher CH_4/O_2 ratios (Figs. 4.4.2, 4.4.5, 4.4.7

TABLE 4.4.1. Results of the Oxy-CO₂ and Steam Reforming of Methane over the Catalyst with Co/Ni Ratio of 0.17 and 1.0 at Different CO₂/H₂O Ratios and Temperatures, [CH₄/O₂ = 2.09 ± 0.01, CH₄/(O₂ + 0.5CO₂ + 0.5 H₂O) = 1.81, CH₄/(CO₂ + H₂O) = 6.0 ± 0.2 and GHSV = 4.7 x 10⁴ cm³ g⁻¹ h⁻¹]

CO ₂ /H ₂ O ratio	Catalyst with Co/Ni ratio = 0.17		Catalyst with Co/Ni ratio = 1.0	
	CH ₄ conversion (%)	H ₂ /CO ratio	CH ₄ conversion(%)	H ₂ /CO ratio
<u>Temp.: 800°C</u>				
0.0	93.8	2.22	93.2	2.26
0.78	94.5	1.97	94.6	2.00
1.36	93.6	1.91	92.9	1.86
2.57	93.6	1.85	93.1	1.77
∞	94.7	1.74	94.5	1.74
<u>Temp. : 850°C</u>				
0.0	98.1	2.23	98.2	2.16
0.78	97.0	1.95	97.5	1.97
1.36	96.7	1.86	96.9	1.86
2.57	96.9	1.79	97.1	1.81
∞	97.5	1.71	97.9	1.73

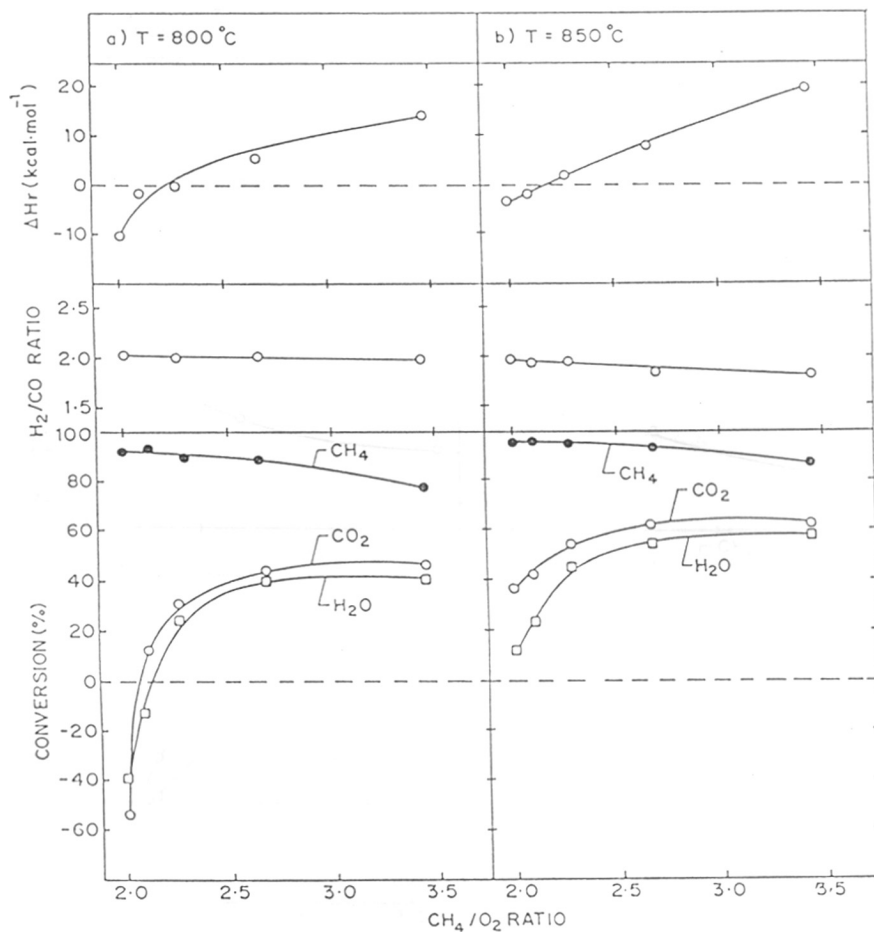


Fig. 4.4.7.: Effect of CH₄/O₂ feed ratio on the conversion, selectivity, H₂/CO product ratio and net heat of reaction (ΔH_r) in the simultaneous oxy-CO₂ and steam reforming of methane over the catalyst with Co/Ni ratio of 0.17 at 800° and 850°C [$\text{CH}_4/(\text{O}_2 + 0.5\text{CO}_2 + 0.5\text{H}_2\text{O}) = 1.8$, $\text{CO}_2/\text{H}_2\text{O} = 1.0$, $\text{GHSV} = 4.6 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$].

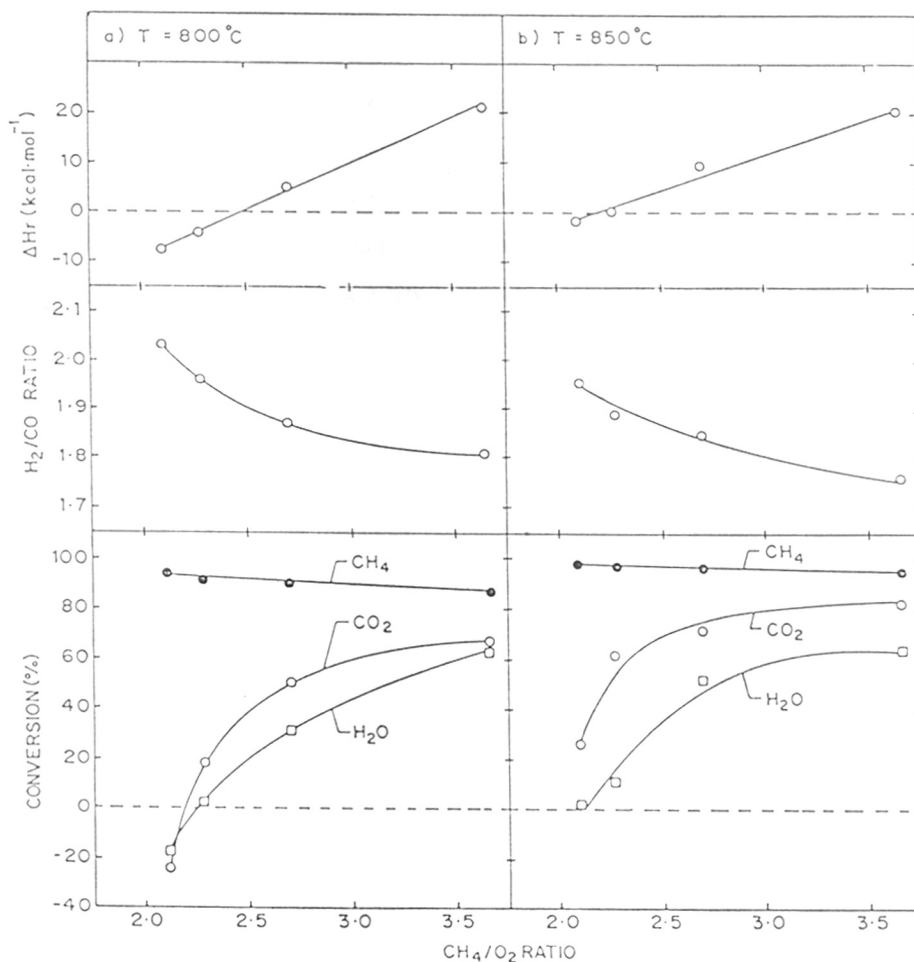


Fig. 4.4.8.: Performance of the catalyst with Co/Ni ratio of 1.0 in the simultaneous oxy- CO_2 and steam reforming of methane at different temperatures and CH_4/O_2 ratios [$\text{CH}_4/(\text{O}_2 + 0.5(\text{CO}_2 + 0.5\text{H}_2\text{O})) = 1.8$, $\text{CO}_2/\text{H}_2\text{O} = 1.0$ and $\text{GHSV} = 4.6 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$]

and 4.4.8) or only when most of the O_2 present in the reaction mixture is converted, leaving enough unreacted methane. These observations indicate that, in all the three processes, the oxidative conversion for methane (reaction 1) is faster than the CO_2 and/or steam reforming reactions (reactions 2 and 3). It is, therefore, interesting to know whether these exothermic (oxidative conversion) and endothermic (CO_2 and/or steam reforming) reactions over the catalyst occur in series (i.e. the oxidative conversion occurring in the initial small part of the catalyst and the CO_2 and/or steam reforming reactions occurring in the next or remaining part of the catalyst) or in parallel (i.e. all the reactions occurring simultaneously throughout the catalyst). A further detailed investigation, particularly using a larger amount of catalyst, is necessary for a clear understanding of the above.

Nevertheless, because of the presence of CO_2 and/or steam along with O_2 in the feed and also the catalyst showing high activity for both steam and CO_2 reforming reactions at higher temperatures ($\geq 800^\circ C$), for GHSV as high as that ($4-5 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$) used in the present study (22), at least a significant part of the CO_2 and/or steam reforming reactions are expected to occur simultaneously with the oxidative conversion reaction.

Although, the oxidative conversion of methane to CO and H_2 is mildly exothermic ($\Delta H_r = -5.4 \text{ kcal mol}^{-1}$), a large amount of heat is expected to be produced in a small catalyst volume because of the high conversion at a very low contact time. However, because of the presence of the CO_2 and/or H_2O along with O_2 , the heat produced is absorbed in the highly endothermic CO_2 and/or steam reforming reactions, thus setting a buffer action on the reaction temperature and thereby avoiding a temperature rise above a certain temperature, depending upon the feed composition and/or other process conditions. This is of great practical importance for avoiding temperature run-away and/or formation of hot spots in the reactor, as safety is major concern for any process application. Because of the coupling of the exothermic oxidative conversion and endothermic CO_2 and/or steam reforming reactions, the oxy- CO_2 and/or steam reforming processes can be made mildly exothermic, thermoneutral or mildly exothermic by manipulating the process conditions, particularly the reaction temperature and CH_4/O_2 feed ratio (Figs. 4.4.2, 4.4.5, 4.4.7 and 4.4.8). The process endothermicity can be increased by increasing the temperature and/or CH_4/O_2 ratio. Moreover, H_2/CO product ratio in these processes can be varied and syngas with a desired H_2/CO ratio can be obtained by manipulating the relative

concentrations of methane, O₂ and CO₂ and/or steam in the feed (Figs. 4.4.2, 4.4.5, 4.4.7 and 4.4.8 and Table 4.4.1). Also, in the oxy-CO₂ and steam reforming process, a formation of side products can be totally avoided and 100% selectivity for both CO and H₂ in the conversion methane to syngas can be obtained. This of great practical importance for avoiding the formation of environmentally undesirable side product, such as CO₂ (which is responsible for global warming).

4.4.3.2. Effect of Co/Ni Ratio of the Catalyst

Our earlier studies (22) revealed that the presence of cobalt in the catalyst, similar to that used in the present investigation has a beneficial effect on the filamental carbon formation, which is drastically decreased with increasing the Co/Ni ratio of the catalyst. The catalyst also showed an improved performance in the CO₂ and steam reforming of methane and also in the simultaneous CO₂ and steam reforming of methane because of the addition of cobalt; the best performance was observed for the Co/Ni ratio of 0.17. Similarly, the optimum Co/Ni ratio of the catalyst for the oxy-CO₂ and oxy-steam reforming processes is found to be 0.17 (Figs. 4.4.1, 4.4.3 and 4.4.4).

For the simultaneous oxy-CO₂ and oxy-steam reforming processes, the Co/Ni ratio of the catalyst showed no significant effect on the methane conversion and H₂/CO product ratio (Fig. 4.4.6). The performance of the catalyst with two different Co/Ni ratios (0.17 and 1.0) in this process at different process conditions is also comparable (Figs. 4.4.7, 4.4.8 and Table 4.4.1). Hence, because of its lower filamental carbon activity, the catalyst with higher Co/Ni ratio is more preferable. The effect of Co/Ni ratio of the catalyst on the conversion of H₂O and CO₂ shows a strong dependence on the process conditions (Fig.6). This is because of the complex nature of the oxy-CO₂ and steam reforming process

4.4.4. CONCLUSIONS

From the studies on the oxy-CO₂ and/or steam reforming processes over the Co_xNi_{1-x}O/MgO/SA-5205 catalysts (x = 0.0 - 0.5) at different process conditions, following important conclusions have been drawn.

- 1) Because of the addition of cobalt to the catalyst, in addition to having a better stability against filamental carbon formation, the catalyst showed improved performance in the oxy-CO₂ reforming and oxy-steam reforming processes; the optimum Co/Ni ratio in the catalyst for its best performance in these processes is 0.17.
- 2) In case of the simultaneous oxy-CO₂ and steam reforming process, the methane conversion and H₂/CO product ratio is not influenced significantly by the addition of cobalt to the catalyst. Hence, for this process, the catalyst with higher Co/Ni ratio (which has higher stability against filamental carbon formation) is more preferable and it is a highly promising catalyst for this process.
- 3) In the oxy-CO₂ and/or steam reforming processes over the catalyst (with Co/Ni ratio of 0.17 and 1.0), methane can be converted to CO and H₂ with high conversion (above 95%) and high selectivity (even 100%), depending upon the process) at low contact time or high space velocity ($5 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$).
- 4) In the oxy-CO₂ and/or steam reforming processes, the H₂/CO product ratio can be varied and a desired H₂/CO product ratio can be obtained by manipulating the process conditions, particularly the feed compositions (i.e. relative concentrations of CH₄, O₂, CO₂ and /or steam in the feed). Any of these processes can be made mildly exothermic, thermoneutral or mildly endothermic by manipulating the process conditions (particularly, the temperature and CH₄/O₂ ratio in the feed).

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1. U.S. Patent 5,338,488 [Aug. 16,1994]

"Process for the production of synthesis gas by oxidative conversion of methane (or natural gas) using composite catalyst containing transitional and alkaline earth metal oxides"

V.R.Choudhary, A.M.Rajput, S.D.Sansare, B.Prabhakar and **A.S.Mamman**

2. U.S.Patent 5,756,421 [May 26, 1998]

Composite catalyst containing transitional and alkaline earth metal oxides useful for oxidative conversion of methane (or natural gas) to carbon monoxide and hydrogen (or synthesis gas)

V.R.Choudhary, A.M.Rajput, S.D.Sansare, B.Prabhakar and **A.S.Mamman**

3. U.S. Patent Application No. 08/372650 [1994]

"Process for oxidative conversion of methane or natural gas to syngas in an energy efficient manner, using an improved supported catalyst containing nickel and cobalt"

V.R.Choudhary, B.S.Uphade, **A.S.Mamman**, A.M.Rajput

4. U.S. Patent Application No. 08/359035 [1994]

"Process for the preparation of an improved supported catalyst containing nickel and cobalt, with or without noble metals, useful for the oxidative conversion of methane, natural gas and biogas to syngas"

V.R.Choudhary, B.S.Uphade, **A.S.Mamman**, A.M.Rajput

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