Steam and Oxysteam Reforming of Methane to Syngas over $Co_xNi_{1-x}O$ Supported on MgO Precoated SA-5205

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Catalytic steam and oxysteam reforming of methane to syngas studied involves coupling of exothermic oxidative conversion and endothermic steam-reforming processes over $Co_xNi_{1-x}O$ ($x = 0.0-0.5$) supported on MgO precoated commercial low surface area ($< 0.01\ m^2\ g^{-1}$) macroporous silica-alumina SA-5205 catalyst carrier. The influence of the Co/Ni ratio of the catalyst on its performance in steam and oxysteam reforming processes (at 800 and 850°C) was studied. For the steam reforming process, the Co/Ni ratio influences strongly on the methane and steam conversion and CO selectivity and product H_2/CO ratio, particularly at lower temperature. When the Co/Ni ratio is increased, the methane and H_2O conversion and CO selectivity are decreased markedly. For the oxysteam reforming process, the influence of the Co/Ni ratio on the performance is smaller and depends on process conditions. When the Co/Ni is increased, the methane conversion passes through a maximum at the Co/Ni ratio of 0.17. The influence of the reaction temperature (800 and 850°C) and CH_4/O_2 and CH_4/H_2O ratios on the conversion, selectivity, H_2/CO product ratio, and net reaction heat (ΔH_r) was studied in the oxysteam reforming (at space velocity of 47,000 $cm^3 \cdot g^{-1} \cdot h^{-1}$) over the catalyst with an optimum Co/Ni ratio (0.17) and a higher Co/Ni ratio (1.0). The oxysteam reforming process involves coupling the exothermic oxidative conversion of methane and the endothermic methane steam reforming reactions, making the process highly energy-efficient and nonhazardous. This process can be made thermoneutral, mildly exothermic, and mildly endothermic by manipulating process conditions.

Introduction

Synthesis gas (a mixture of CO and H_2) is a versatile feedstock for the ammonia, methanol, and Fischer-Tropsch synthesis processes, and for a number of carbonylation, hydrogenation or reduction processes as well. Currently, synthesis gas is produced from methane mostly by steam reforming (Kirk and Othmers et al., 1980; Elvers et al. 1989). This process suffers from severe limitations, such as very high energy requirements, high H_2/CO ratio (which is not suitable for methanol and Fischer-Tropsch synthesis), poor selectivity for carbon monoxide, and high capital and operating costs, making the process uneconomical for upgrading natural gas. Catalytic selective oxidation of methane to syngas (Bhardwaj and Schmidt, 1995; Pena et al.; 1996), which is a mildly exothermic ($\Delta H = -5.4$ kcal$\cdot$mol^{-1}) process, is free from almost all of the limitations associated with the steam re-forming process. Hence, the oxidative conversion of methane to syngas offers an alternative route by which syngas can be produced more energy efficiently and economically from methane.

Since the last decade, worldwide efforts by many have been made, including our group, for the oxidative conversion of methane to syngas. A number of studies on the partial oxidation of methane to syngas over the noble metals and Ni-and/or Co-containing catalysts (Bhardwaj and Schmidt, 1995; Pena et al., 1996) have been reported. This process, particularly at a very low contact time (< 1.0 ms) is of great practical importance (Choudhary et al., 1992a–e, 1993, 1997; Lapszewicz and Jiang, 1992, 1993; Hickman and Schmidt, 1992, 1993; Hickman et al., 1993).

In all the preceding studies, the amount of catalyst used was very small (≤ 20 mg), and hence there was no serious

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problem for the removal of heat from the reactor. But when a large amount of catalyst (1.0 g) was used, it was extremely difficult to control the reaction because of the limitations imposed by heat removal from the reactor (Choudhary et al., 1994a). In this process, a very low contact time coupled with the high conversion ($\geq 90\%$) results in the 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 for some reason can result in a drastic increase in the heat produced due to the combustion of methane to CO_2 and water (which is highly exothermic), thus making the process control still more difficult and/or leading to process runaway. In spite of the fact that the partial oxidation of methane to CO and H_2 is mildly exothermic ($\Delta H_r = 5.4$ kcal·mol^{-1}), the process is highly hazardous, and hence difficult to practice. 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 (Choudhary et al., 1995a, 1998a), or CO_2 reforming of methane (Ashcroft et al., 1991; Choudhary et al., 1995b; 1998a, Choudhary and Mamman 1998), or with both (Choudhary et al., 1994b, 1996, 1998a, 1998b); the exothermic and endothermic reactions could be coupled successfully, making the process not only highly energy efficient but also nonhazardous and safe to operate.

In our earlier studies (Choudhary, et al., 1997b), NiO supported on MgO precoated low surface area macroporous silica-alumina catalyst carrier showed high activity and selectivity in the oxidative conversion of methane to syngas. This catalyst also showed very good performance in oxy-steam and/or CO_2 re-forming of methane of syngas (Choudhary et al., 1998a). An addition of cobalt to nickel-containing Yb_2O_3, ZrO_2, and ThO_2 catalysts caused a drastic reduction in the filamental carbon formation on them, but a small decrease in the selectivity for both CO and H_2 in the oxidative conversion of methane to syngas (Choudhary et al., 1997a, 1998c). Also, the addition of cobalt to the supported NiO and NiO-MgO catalysts caused a drastic reduction in the filamental carbon formation in the CO_2 re-forming (Choudhary et al., 2000) and oxy-CO_2 re-forming (Choudhary and Mamman, 1998) of methane over these catalysts. It is therefore of great practical interest to study the effect of cobalt addition (which drastically reduces the carbon formation) to the previously mentioned supported nickel oxide catalyst on its performance (activity and selectivity) in the steam re-forming and also in the simultaneous steam re-forming and oxidative conversion of methane to syngas at low contact time. The present work was undertaken for this purpose and also for thoroughly evaluating a performance of the Co-containing supported NiO-MgO catalyst in both the steam re-forming and oxy-steam re-forming processes at different process conditions.

Experimental Studies

Supported $CO_xNi_{1-x}O$ (14.0 ± 0.5 wt. %)/MgO/ (7.2 wt. %)/SA-5205 ($x = 0.0$, 0.05, 0.15, 0.29, and 0.5) catalysts were prepared by depositing mixed nitrates of Ni and Co with desired Co/Ni ratio (0.0, 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 support, obtained from M/S Norton Co.) precoated with MgO, using an incipient wetness impregnating technique, followed by drying and decomposing (or calcining) in air at 900°C for 4 h. 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 m^2·g^{-1}, 54%, 0.35 cm^3 g^{-1}, and 200 μm, respectively.

The catalyst was characterized for its surface area by the single-point BET method, using a Monosorb Surface Area Analyzer (Quanta Chrome Corp.). The catalyst was also characterized by its temperature programmed reduction (TPR) from 100°C to 900°C with a linear heating rate of 20°C·min^{-1} in a flow of H_2-Ar (3.7 mol % H_2) mixture (space velocity = 6,000 cm^3·g^{-1}·h^{-1}) in a quartz reactor (ID 4 mm) having a low dead volume.

The catalytic steam re-forming and simultaneous steam re-forming and partial oxidation of methane to syngas reactions over the catalysts were carried out at the atmospheric pressure in a continuous-flow quartz reactor (ID 9 mm) packed with 0.3 g catalyst. The feed was a mixture of pure methane ($> 99.95\%$) O_2 (99.99%), and/or steam. Water was added to the feed using a SAGE syringe pump and a specially designed evaporator. The reaction temperature was measured by a Chromel-Alumel thermocouple located in the center of the catalyst bed. Before carrying out the reaction, the catalyst was heated *in situ* at 900°C in a flow (50 cm^3·min^{-1}) of moisture-free nitrogen for 1 h. 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, and/or O_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 Spherocarb column and He as a carrier gas. The conversion/selectivity data were collected after attaining the reaction steady state (after a reaction period of 30 min). The runs showing material balance for C, H, and O with an error above 6% were rejected.

Results and Discussion

The Co/Ni ratio strongly infuences both the surface area and degree of reduction in the TPR of the supported $CO_xNi_{1-x}O$-MgO catalyst (Figure 1). The surface area of the support (SA-5205) is negligibly small (< 0.01 m^2·g^{-1}). Hence, the surface area of the catalyst (Figure 1) is due to the active catalyst mass $Co_xNi_{1-x}O$-MgO deposited on the support.

The surface area is decreased markedly by increasing the Co/Ni ratio. This reveals that the catalyst is sintered more and more due to its crystal growth when more and more cobalt is present. However, the degree of reduction (percent reduction of NiO and CoO present in the catalyst by a reaction: CoO or $NiO + H_2 \rightarrow CO$ or $Ni + H_2O$) of the catalyst is increased by increasing the Co/Ni ratio. The degree of reduction was estimated from knowledge of the concentrations of CoO and NiO in the catalyst, the amount of H_2 consumed in the TPR, and assuming the reaction stoichiometry.

The peak maximum temperature of the TPR curves for all the catalysts was ≥ 900°C and the TPR curves are quite similar to that observed for the catalyst without cobalt (Choudhary et al., 1997b, 1998a) and also for a NiO-MgO solid solution (Highfield et al. 1983; Parmaliana et al., 1990). This indicates

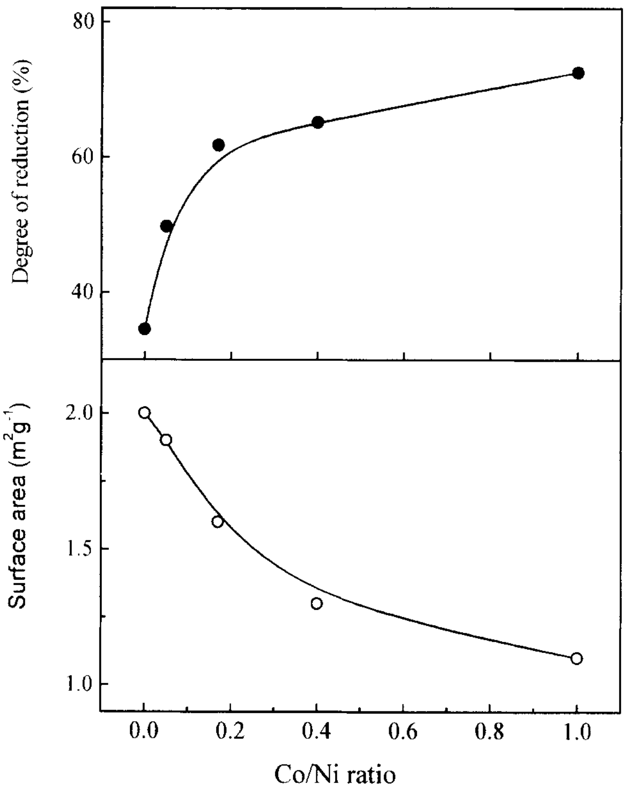

Figure 1. Influence of Co/Ni ratio of the catalyst on its top surface area and bottom degree of reduction in the TPR.

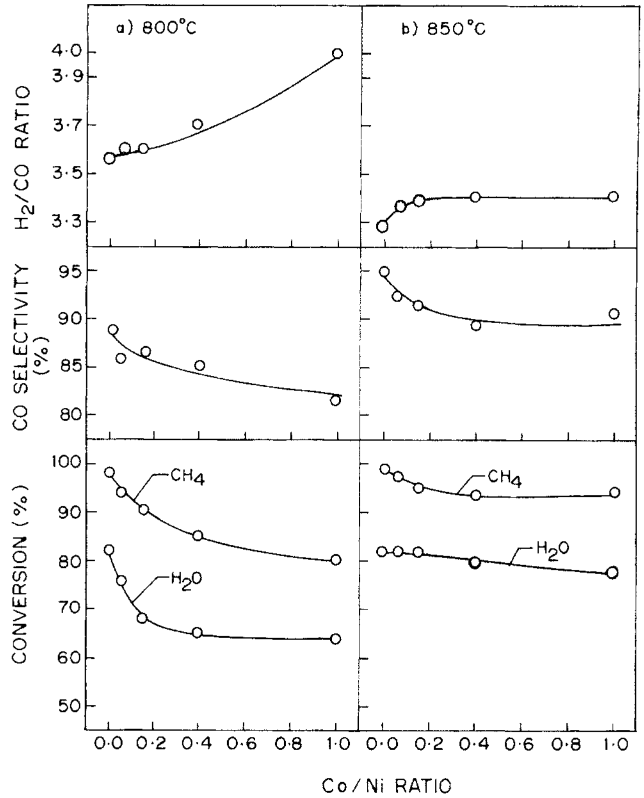

Figure 2. Influence of Co/Ni ratio in the catalyst on its performance in the steam reforming of methane at 800 and 850°C.

H_2O/CH_4 feed ratio = 1.54 and GHSV = 2.3×10^4 $cm^3 \cdot g^{-1} \cdot h^{-1}$.

the presence of NiO, CoO, and MgO as their solid solution in the catalyst.

In both the steam re-forming and oxy-steam re-forming processes, the NiO and CoO present at the surface and close to the surface of the catalyst are reduced by their reaction with methane in the initial short period. The steady catalytic activity in both the processes was obtained within a period of 20–25 minutes at 800°C.

Steam Reforming of Methane

Figures 2 and 3 show the influence of the Co/Ni ratio of the catalyst and process variables on the conversion of methane and water, CO selectivity, and H_2/CO product ratio in the steam re-forming of methane.

When the Co/Ni ratio is increased, the conversion of both the reactants (methane and water) and also the CO selectivity are decreased and the H_2/CO ratio in the product is increased due to a decrease in the production of CO relative to that of H_2. The influence is particularly stronger at the lower temperature (at 800°C). At the higher temperature (850°C), the influence of Co/Ni ratio is very small particularly when the Co/Ni ratio is above 0.17. The decrease in the CO selectivity and/or increase in the H_2/CO ratio by increasing the Co/Ni ratio (Figure 2) indicates that along with steam re-forming of methane.

$$CH_4 + H_2O \rightarrow CO + 3H_2 - 54.2\ \text{kcal} \cdot \text{mol}^{-1} \qquad (1)$$

water gas shift reaction,

$$CO + H_2O \rightarrow CO_2 + H_2 + 8.2\ \text{kcal} \cdot \text{mol}^{-1} \qquad (2)$$

occurs to an increasing extent.

When the temperature is increased, the conversion of both methane and water is increased, the CO selectivity is also increased, and consequently the H_2/CO ratio is decreased (Figure 3a). The observed CO selectivity below 100% (Figures 2 and 3) indicates the occurrence of the water gas shift reaction simultaneously with steam re-forming. The occurrence of water gas shift reaction (Reaction 2) relative to that of steam reforming (Reaction 1) is, however, decreased by increasing the temperature.

The conversion of methane and water is decreased appreciably as expected, the CO selectivity is also decreased, and consequently the H_2/CO ratio is increased with an increase in the GHSV at 800°C and H_2O/CH_4 feed ratio of 1.15 (Figure 3b). The results indicate that the water gas shift reaction (Reaction 2) occurs to an appreciable extent at the higher GHSV.

When the steam/methane ratio (at 800°C and GHSV = 45,000 $cm^3 \cdot g^{-1} \cdot h^{-1}$) is increased, the methane conversion is increased, the conversion of water is decreased, the CO selectivity is decreased sharply, and consequently the H_2/CO ratio is increased sharply (Figure 3c). At the higher H_2O/CH_4

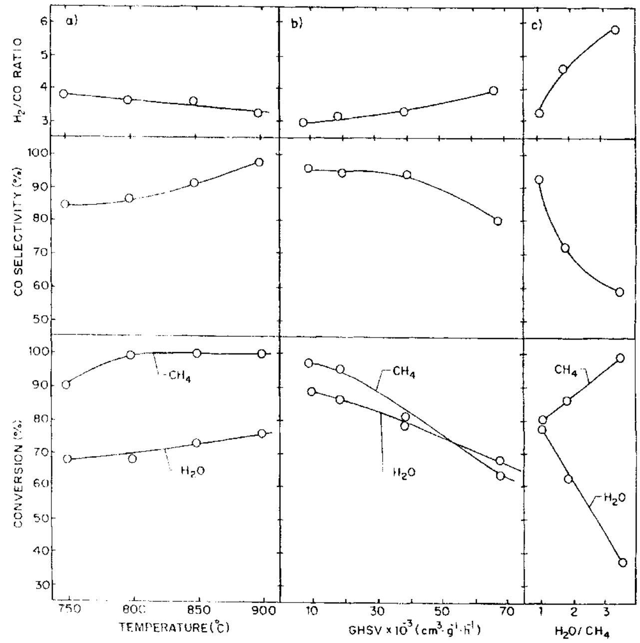

Figure 3. Influence of (a) reaction temperature ($H_2O/CH_4 = 1.56$ and GHSV = 2.3×10^4 cm^3·g^{-1}·h^{-1}), (b) space velocity (at 800°C and $H_2O/CH_4 = 1.15$), and (c) H_2O/CH_4 ratio (at 800°C and GHSV = 4.5×10^4 cm^3·g^{-1}·h^{-1}) on the conversion, CO selectivity, and H_2/CO product ratio in the steam reforming of methane over the catalyst with a Co/Ni ratio of 0.17.

ratio, the water gas shift reaction (Reaction 2) occurs to a very appreciable extent.

It is evident from the results (Figure 3) that the side reaction (Reaction 2) is more predominant at a lower temperature, higher space velocity, and higher H_2O/CH_4 feed ratio.

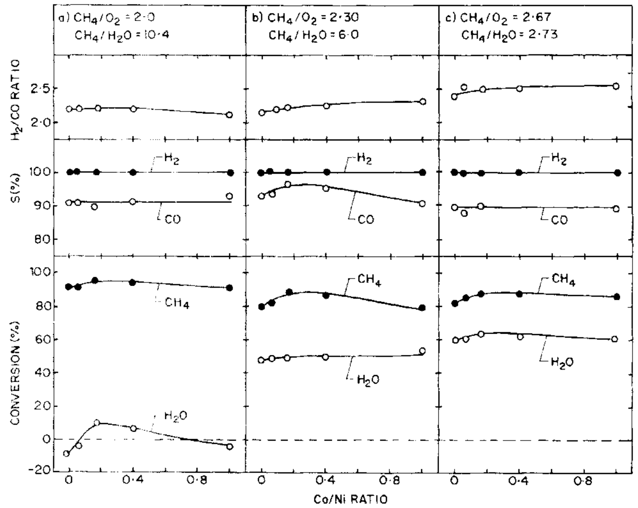

Figure 4. Effect of Co/Ni ratio of the catalyst on its performance in the oxysteam reforming of methane at 800°C (GHSV = 4.7×10^4 cm^3·g^{-1}·h^{-1}).

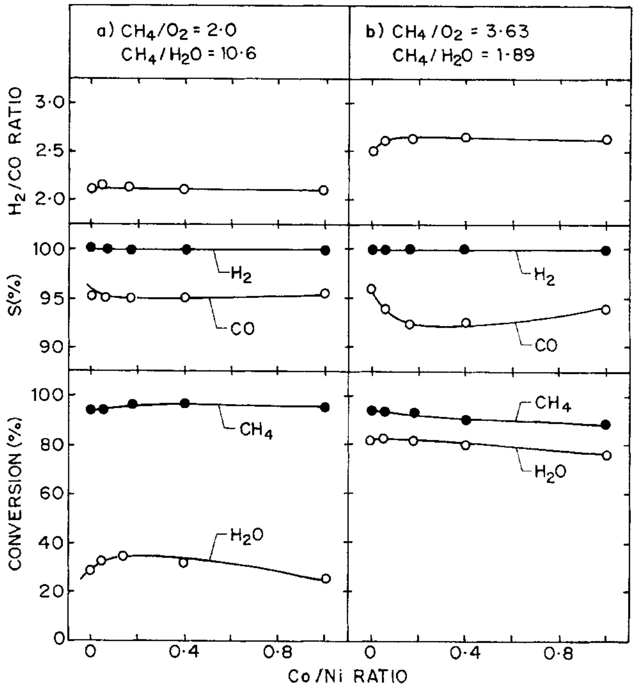

Figure 5. Effect of Co/Ni ratio of the catalyst on its performance in the oxysteam reforming of methane at 850°C (GHSV = 4.7×10^4 cm^3·g^{-1}·h^{-1}).

The strong influence of Co/Ni ratio and GHSV observed shows that the steam re-forming and water gas shift reactions are not at equilibrium. The CO selectivity in the process is controlled kinetically.

In the steam re-forming of methane over all the catalysts, the carbon deposited on the catalyst was negligibly small. When the steam re-forming of methane over the catalyst with a Co/Ni ratio of 0.17 (at 850°C, $CH_4/H_2O = 1.54$, and GHSV = 23,000 cm^3·g^{-1}·h^{-1}) was carried out continuously for a period of 15 h, there was no significant change in the conversion of both the reactants or in the CO selectivity. Also, there was no significant increase in the pressure drop across the catalyst bed. Microanalysis of the catalyst after the reaction showed the presence of only 0.1 wt. % carbon on the catalyst.

Oxysteam Reforming of Methane

The effect of the Co/Ni ratio of the catalyst at different temperatures (800 and 850°C) and CH_4/O_2 and CH_4/H_2O feed ratios are shown in Figures 4 and 5. Results showing the influence of the Co/Ni ratio of the catalyst and CH_4/O_2 (or CH_4/H_2O) ratio [at constant $CH_4/(O_2+0.5H_2O)$ ratio of 1.82] at different temperatures (800° and 850°C) on the conversion, selectivity, and net heat of reaction (ΔH_r) in the oxysteam reforming process over the catalyst with the optimum Co/Ni ratio (0.17) are presented in Figure 6. The results for the catalyst with the Co/Ni ratio of 1.0 are presented in Table 1. The net heat of reaction was estimated by subtracting the heat of formation (at reaction conditions) of the reactants from that of products formed in the process.

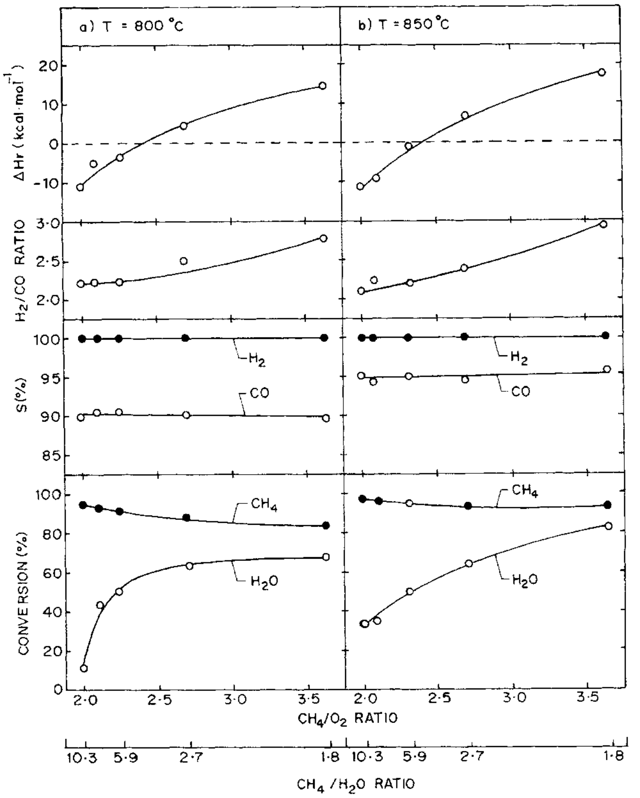

Figure 6. Effect of CH_4/O_2 feed ratio on the conversion, selectivity, H_2/CO product ratio, and net heat of reaction (ΔH_r) in the oxysteam reforming of methane over the catalyst with a Co/Ni ratio of 0.17 at 800 and 850°C [$CH_4/(O_2+0.5H_2O)=1.82$, GHSV $= 4.7\times10^4$ $cm^3\cdot g^{-1}\cdot h^{-1}$].

The results (Figures 4 and 5) reveal that the Co/Ni ratio has a small effect on the conversion, selectivity, and H_2/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 negative conversion of water (Figure 4a) indicates that there is a net formation of water in the process at the lower CH_4/O_2 feed ratio (or at the high CH_4/H_2O). Our earlier studies (Choudhary et al., 2000) showed that the carbon deposition on the catalyst in the CO_2 re-forming of methane is drastically reduced by increasing the Co/Ni ratio. This study shows that in the oxy-steam re-forming of methane, the Co/Ni ratio has only a mild effect on the conversion and CO selectivity (Figures 4 and 5). Hence, the catalyst with high Co/Ni ratio may be preferred in this process, as the loss in the conversion and CO selectivity, if any, could very well be compensated by the drastic reduction in the carbon formation, which is of great practical importance in the methane-to-syngas conversion process. Although we have not observed significant carbon formation on the catalyst, even with lower Co/Ni ratios, for the short durations, when the process is operated for longer periods, the deposition of filamental carbon, particularly at high CH_4/H_2O ratios due to a failure of the process control, could be a serious problem. Hence, we recommend the use of this catalyst with high Co/Ni ratio for the oxysteam reforming process.

Table 1. Oxysteam Reforming of Methane Over the Catalyst with Co/Ni Ratio of 1.0

Temp.	Feed Ratio		Conv. (%)		CO Select.	H_2/CO	Net Heat of React., ΔH_r
(°C)	CH_4/O_2	CH_4/H_2O	CH_4	H_2O	(%)	ratio	(kcal·mol⁻¹)
800	2.0	10.3	91.4	−4.5	93.1	2.15	−17.5
850	2.0	10.3	96.1	25.4	95.7	2.12	−6.6
800	2.3	5.9	90.1	54.9	91.5	2.3	−3.8
850	2.3	5.9	95.8	55.1	95.2	2.2	−1.6
800	2.7	2.7	88.7	62.4	88.8	2.55	+3.3
850	2.7	2.7	95.6	70.8	93.7	2.46	+6.7
800	3.6	1.8	82.4	64.7	88.3	2.75	+12.7
850	3.6	1.8	76.5	76.5	93.2	2.63	+18.9

Note: GHSV = 5.1×10^4 $cm^3\cdot g^{-1}\cdot h^{-1}$

When the CH_4/O_2 ratio is increased (or the CH_4/H_2O ratio is decreased), the following important observations can be made (Figure 6 and Table 1):

- There is a small but continuous decrease in the methane conversion, but an appreciable increase in the water conversion.
- The CO selectivity for the catalyst with a Co/Ni ratio of 1.0 (Table 1) is decreased, but little or no change in the selectivity for the catalyst with Co/Ni ratio of 0.17 is observed.
- The H_2/CO product ratio is increased appreciably.
- The process endothermicity is increased markedly, transforming the mildly exothermic process (at the lower CH_4/O_2 ratios) into the mildly endothermic one (at the higher CH_4/O_2 ratios).

These results indicate that in the oxysteam reforming process the steam reforming of methane (Reaction 1) occurs along with the oxidative conversion of methane (Reaction 3):

$$CH_4+0.5O_2\rightarrow CO+2H_2+5.4\,\text{kcal}\cdot\text{mol}^{-1} \qquad (3)$$

In the oxidative conversion of methane, there is also the possibility of the combustion of methane converting to CO_2 and water. The CO_2 and water thus formed can react with methane over the catalyst to form CO and H_2.

The observed CO selectivity is found to be less than 100% (Figures 4 and 6 and Table 1). The H_2/CO ratio is increased by decreasing the CH_4/H_2O ratio (Figure 6 and Table 1). These observations suggest that the water gas shift reaction (Reaction 2) also occurs simultaneously with the oxidative conversion and steam reforming reactions (Reactions 1 and 3). The observed lower CO selectivity, particularly when the CH_4/H_2O ratio is high, may be due to the complete combustion of part of the methane.

It can be noted that the performance of the catalyst with high Co/Ni ratio (Table 1) is comparable to that with the optimum Co/Ni ratio. Hence, the catalyst with a high Co/Ni ratio is more preferred because of its much higher stability against carbon deposition (Choudhary et al., 2000) in the methane-to-syngas conversion by the oxysteam reforming process.

Coupling of endothermic steam reforming with exothermic oxidative conversion of methane to syngas

In oxysteam reforming, the conversion of O_2 was always above 98% at all the process conditions. When the CH_4/O_2 feed ratio is increased, there is a small decrease in the conversion of methane, but a large increase in the conversion of steam. A high steam conversion is observed only for the higher CH_4/O_2 ratios (Figure 6 and Table 1) or only when most of the O_2 present in the reaction mixture is converted, leaving enough unreacted methane. These observations indicate that, in the oxysteam reforming, the oxidative conversion of methane (Reaction 3) is faster than the steam reforming reaction (Reaction 1). It is therefore interesting to know whether these exothermic (oxidative conversion) and endothermic (steam re-forming) reactions over the catalyst occur in series (that is, the oxidative conversion occurring in the first few layers of the catalyst particles and the steam re-forming reaction occurring in the next or remaining part of the catalyst) or in parallel (that is, both the reactions occurring simultaneously throughout the catalyst). A further detailed investigation, particularly one using a larger amount of catalyst, is necessary for a clear understanding of the preceding. Nevertheless, since the catalyst showed high activity for the steam re-forming reaction at higher temperatures (≥ 800°C), for GHSV as high as that (47,000 or 51,000 $cm^3 \cdot g^{-1} \cdot h^{-1}$) (Figure 3), the steam reforming reaction is expected to occur simultaneously with the oxidative conversion reaction, at least at the higher temperatures.

Although the oxidative conversion of methane to CO and H_2 is mildly exothermic ($\Delta H_r = -5.4$ 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 steam along with O_2, the heat produced is absorbed in the highly endothermic steam re-forming reaction, thus setting a buffer-like action on the reaction temperature. Because of this, there is a control on the temperature rise. This is of great practical importance for avoiding temperature runaway and/or formation of hot spots in the reactor, as safety is a major concern for practicing any process. Because of the coupling of the exothermic oxidative conversion and endothermic steam reforming reactions, the oxy-steam re-forming processes can be made mildly endothermic, thermoneutral, or mildly exothermic by manipulating the process conditions, particularly the CH_4/O_2 feed ratio (Figure 6 and Table-1). The process endothermicity can be increased by increasing the temperature and/or CH_4/O_2 ratio. Moreover, the H_2/CO product ratio in this process can be varied between 2 and 3 by manipulating the relative concentrations of methane, O_2, and steam in the feed (Figure 6 and Table 1). Also, as long as the conversion of water is greater than or equal to zero, H_2 selectivity based on methane conversion is always 100%. However, the CO selectivity would be less than 100% because of the water gas shift reaction (Reaction 2) depending upon the reaction conditions (Figures 4–6).

Conclusions

From the studies on the steam reforming and oxysteam reforming processes over $Co_x Ni_{1-x}O$ ($x = 0.0$–0.5) supported on the lower surface area macroporous silica–alumina catalyst carrier, precoated with MgO, the following important conclusions have been drawn:

1. Because of the addition of cobalt to the catalyst, which imparts high stability to the catalyst against filamental carbon formation, the catalyst showed inferior performance (both the conversion and selectivity are decreased) in the steam reforming process. However, the catalyst showed improved performance at the optimum Co/Ni ratio of 0.17, and also a relatively smaller effect on the conversion and selectivity in the oxysteam reforming process due to the addition of cobalt. Hence, because of its high stability against carbon formation, the catalyst with a high Co/Ni ratio is preferable, and it is a highly promising catalyst.
2. In the oxysteam reforming process over the catalyst (with Co/Ni ratio of 0.17 and 1.0), methane can be converted into CO and H_2 with a high conversion (above 95%) and high selectivity (H_2 selectivity = 100%, and CO selectivity ≈ 95%) at a very high space velocity (51,000 $cm^3 \cdot g^{-1} \cdot h^{-1}$ at a temperature ≥ 800°C). The H_2/CO product ratio can be varied between 2 and 3 by varying the relative concentrations of CH_4, O_2, and steam in the feed.
3. In the oxysteam reforming process over the catalyst (at ≥ 800°C), the endothermic (steam reforming) and exothermic (oxidative conversion) reactions are at least partly coupled by their simultaneous occurrence over the same catalyst. This makes the process highly energy efficient and also safer than the oxidative methane-to-syngas conversion process. The oxysteam reforming process can be made mildly exothermic, thermoneutral, or mildly endothermic by manipulating the feed composition (concentration of steam and O_2 relative to that of methane), and hence can be operated in a safe manner, requiring little or no external energy.

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