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Catalytic Partial Oxidation of Methane to Synthesis Gas over Ni-Based Catalysts

I. Catalyst Performance Characteristics

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The catalytic partial oxidation of methane to synthesis gas was studied over various Ni-based catalysts. It was found that, in contrast to conventional Ni catalysts which show continuous deactivation with time on stream, the Ni/La_2O_3 catalyst exhibits good activity and excellent stability, using the stoichiometric ratio of CH_4/O_2 (=2). Kinetic results indicate that the reaction over the Ni/La_2O_3 catalyst follows mainly the sequence of total oxidation to CO_2 and H_2O, followed by reforming reactions to synthesis gas, while CO formation via the direct route is observed at very low oxygen partial pressures. Chemisorption and FTIR studies show that the enhanced stability of the Ni/La_2O_3 catalyst is related to decoration of the Ni crystallites with lanthanum species, primarily oxycarbonates, which favor removal of excess carbon deposition and impart the catalyst its stability characteristics.

1. INTRODUCTION

The catalytic partial oxidation of methane to synthesis gas (CPO process) has recently received the attention of many research groups (1–22). This is because the CPO process for syngas formation offers many advantages over the conventional steam reforming process, namely: (1) the formation of synthesis gas with lower H_2/CO ratio which is suitable for use in production of methanol and synthetic fuels; (2) it is mechanically simpler than the steam reforming process, since it is completed within a single train, without need of any externally fired heaters; (3) there is no production and release of undesirable emissions (CO_2, SO_x, NO_x); and (4) the CPO process exhibits high activity and selectivity for synthesis gas formation.

Two groups of catalysts have been reported to be active and selective towards partial oxidation of methane to synthesis gas, Ni-based catalysts (4–9) and noble metal-based catalysts (10–18), particularly Rh-based catalysts, which are found to exhibit high activity/selectivity with good long-term stability. However, considering the aspects of high-cost and limited availability of noble metals, it is more practical, from the industrial standpoint, to develop alternative catalysts, e.g. Ni-based catalysts, which exhibit stable operation for extended periods of time. Partial oxidation of methane to synthesis gas over a Ni/Al_2O_3 catalyst was studied in detail by Lunsford and his co-workers (4) in the temperature range of 450–900°C. They reported that CO selectivity approaching 95% and virtually complete conversion of methane can be achieved at temperatures higher than 700°C. It was found, however, that stable operation is not sustainable unless an amount of oxygen larger than the stoichiometric requirement (i.e. $O_2/CH_4 > 0.5$) is supplied.

The deposition of carbon on supported Ni catalysts during CPO of methane was investigated by Claridge *et al.* (7), who showed that both whisker and “encapsulate” forms of carbon are present on the catalyst. Negligible carbon deposition occurred on iridium catalysts, even after 200 h.

Nickel supported on calcium aluminate carriers was also studied by Goula *et al.* (8). The variation of the supports lead to catalysts of different surface properties and catalytic performance. The differences in catalytic activity and selectivity were ascribed to a variable degree of reducibility of the surface nickel species. Slagtern and Olsbye (9) investigated the CPO of methane over several mixed oxides with perovskite structure. They found that the Rh-containing catalysts show good activity and stability, while the nickel-type catalysts (perovskite $LaNiO_3$) quickly deactivate due to excess carbon deposition.

In summary, Ni-based catalysts exhibit good activity and selectivity to synthesis gas formation from CH_4/O_2 mixtures. The major problem encountered with Ni-based catalysts is rapid deactivation, mainly due to carbon deposition. In industrial practice, an amount of oxidant larger than the stoichiometric requirement has to be supplied in order to avoid excess coke formation. It is thus of industrial interest to develop an advanced Ni-based catalyst with which

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stable operation can be achieved with a reactant mixture of stoichiometric oxidant to methane ratio.

A recent study, conducted in this laboratory (19–21) shows that high activity for CO_2 reforming of methane to synthesis gas, combined with excellent stability, can be achieved over a nickel catalyst consisting of nickel crystallites appropriately dispersed on La_2O_3 support. In the present study, the Ni/La_2O_3 catalyst was applied in the CPO process, and results showing high activity and excellent long-term stability are reported. For comparison, kinetic results obtained under analogous reaction conditions over several conventional nickel-based catalysts, i.e. Ni/γ-Al_2O_3, $Ni/CaO/\gamma$-Al_2O_3, and Ni/CaO, are also presented. These supports were selected for the following reasons: γ-Al_2O_3 is most often the carrier of choice for this type of catalysts, CaO is often used as an additive to reduce the acidity of γ-Al_2O_3, and CaO is a typical basic support material to be compared with La_2O_3 which is also a basic material.

2. EXPERIMENTAL

2.1. Catalyst Preparation

The supported Ni catalysts, Ni/La_2O_3, Ni/γ-Al_2O_3, Ni/CaO (10 mol%)/γ-Al_2O_3, and Ni/CaO, were prepared by the wet-impregnation method, using $Ni(NO_3)_2$ (Alfa Products) as the metal precursor. The Ni metal loading was invariably 17 wt%. Desired amounts of $Ni(NO_3)_2$ were dissolved in 30 ml of distilled water at 25°C. Then, the support material, La_2O_3 (Alfa Products), or γ-Al_2O_3 (Akzo Chemicals), or CaO (Alfa Products), or CaO (10 mol%)/γ-Al_2O_3, was added to the solution under continuous stirring at the same temperature. The water was evaporated and the residue was dried at 110°C for 24 h. The dried residue was then ground and sieved and was heated at 500°C under N_2 flow for 2 h for complete decomposition of nickel nitrate. After this treatment, the catalyst was reduced at 500°C in H_2 flow for at least 5 h and stored. Before use, the catalyst for further reduced in flowing hydrogen at 750°C for 1 h.

2.2. Kinetic Apparatus

The apparatus employed for kinetic measurements consists of a flow measuring and control system, a heated quartz tube reactor, and an on-line analytical system. Feed flow rates were measured and controlled by thermal mass flow meters. The reactor was a 4-mm ID quartz tube, immersed in an electrically heated furnace. Weighed amounts of catalyst were placed in the middle of the reactor, supported by quartz wool. A chromel–alumel thermocouple, inside a thermowell which run through the catalyst bed was used for temperature measurement and control. Analysis of the feed and of the reaction mixtures was achieved by a gas chromatograph connected on-line to the reactor apparatus via a gas sampling valve. The TC detector was used to analyze H_2, O_2, CO, CH_4, CO_2, and H_2O, separated by a Carbosieve S-II 100/120 mesh column.

Operating conditions with respect to total feed flow rate and average catalyst particle size were defined so as to minimize intraphase and interface transport resistances. Unless otherwise stated, the following conditions, which have been verified to offer performance free of mass and heat transfer resistances (10) were used: 1 portion of catalyst (0.125–0.18 mm in diameter) was diluted with 2–5 portions of α-Al_2O_3, the reactant mixture was heavily diluted with He, up to 94 vol%. The CH_4-to-O_2 partial pressure ratio applied in the present investigation was invariably 2. Contact time was altered by adjusting the total flow rate and amount of catalyst.

2.3. Catalyst Characterization

H_2 and CO chemisorption on Ni catalysts was conducted in a constant-volume high vacuum apparatus (Micromeritics, Accusorb 2100 E). Uptakes of H_2 and CO at monolayer coverage of the Ni particles were used to estimate Ni metal dispersion and particle size, assuming that each surface Ni site chemisorbs one hydrogen atom or one CO molecule (i.e. $H/Ni_{surface} = 1$, $CO/Ni_{surface} = 1$). H_2 and CO adsorption/desorption on Ni catalysts which had experienced different pretreatments was conducted in a flow apparatus which is connected to a quadrupole mass spectrometer (Fisons, SXP Elite 300 H). The signals of CO, CO_2, H_2, and H_2O were constantly monitored during the experiments.

A Nicolet 740 FTIR spectrometer equipped with a DRIFT (diffuse reflectance infrared Fourier transform) cell was used for the study of CO chemisorption, as well as CH_4/O_2 reaction. An IR spectrum obtained under Ar flow was used as the background to which the spectrum, after exposure to CO/Ar mixtures or $CH_4/O_2/Ar$, was ratioed.

A Philips PW 1840 X-ray diffractometer was used to identify the main phases of Ni/La_2O_3 catalysts before and after reaction. Anode CuKα (40 KV, 30 mA, $\lambda = 1.54$ Å) was used as the X-ray source. The catalyst which had been exposed to reaction conditions for a certain period of time was quickly quenched to room temperature and then transferred onto the XRD sample holder for measurements. The nickel particle size was estimated by employing Scherrer's equation following standard procedures (22).

3. RESULTS AND DISCUSSION

3.1. Catalyst Stability

High conversion and selectivity to synthesis gas from CH_4/O_2 mixtures have been obtained over a number of nickel-based catalysts, including those commonly used in the steam reforming process. The major problem encountered with Ni-based catalysts is rapid deactivation by coke formation. In the present study, a nickel-based catalyst

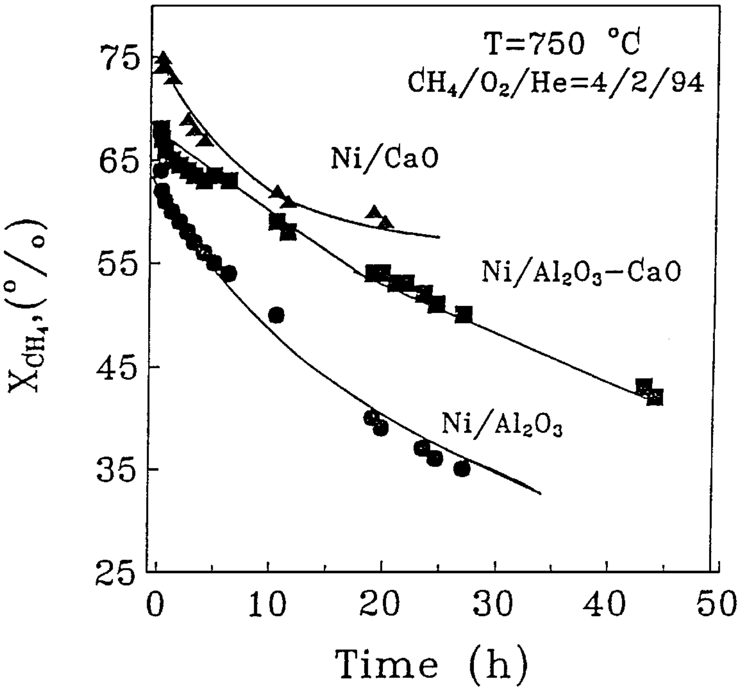

FIG. 1. Alteration of methane conversion as a function of time on stream obtained over Ni/CaO, Ni/Al_2O_3, Ni/CaO (10 mol%)/Al_2O_3 catalysts. $T = 750°C$, $CH_4/O_2/He = 4/2/94$ vol%, metal loading = 17 wt%.

(i.e. Ni/La_2O_3) which exhibits good activity and stability for the catalytic partial oxidation of methane to synthesis gas is described.

The long-term stability obtained over conventional nickel-based catalysts, i.e. Ni/γ-Al_2O_3, Ni/CaO/γ-Al_2O_3, and Ni/CaO, is presented in Fig. 1 which shows the alteration of methane conversion with time on stream. In all catalysts the Ni loading is invariably 17 wt%, while the contact time was adjusted so that conversions were approximately the same and somewhat lower than those expected at thermodynamic equilibrium. The stability experiments were conducted at 750°C with a dilute feed mixture ($CH_4/CO_2/He = 4/2/94$). It is observed that all three conventional Ni catalysts deactivate rapidly with reaction time (Fig. 1). The rate of deactivation follows the order: Ni/γ-Al_2O_3 > Ni/CaO/γ-Al_2O_3 > Ni/CaO. These results are in agreement with previous studies (19, 23) which reveal that Ni-based catalysts are prone to carbon deposition and that the deactivation rate is affected by the nature of the carrier employed, higher deactivation rates observed over carriers of higher acidity.

In contrast to the behavior of the aforementioned conventional Ni-based catalysts, the Ni/La_2O_3 catalyst was found to exhibit stable performance towards synthesis gas formation under the same conditions of partial oxidation of methane. As an even more critical testing of the resistance of the Ni/La_2O_3 catalyst to coke formation, the catalyst was exposed to the reaction mixture of the stoichiometric ratio (i.e. $CH_4/O_2 = 2$) without any gaseous dilution, and stability was tested at 800°C for a prolonged period of time. The contact time used was equal to 1.2×10^{-2} g · s/ml. Figure 2 presents the alteration of methane conversion and CO selectivity during 100 h of CPO reaction. It is shown that methane conversion increases during the initial 5 h of reaction while it remains stable as the reaction proceeds for over 90 h. Thus, for the conditions mentioned previously, methane conversion was equal to 79%, while the CO selectivity had approached the value of 83%.

3.2. *Studies of Catalytic Activity and Selectivity*

High methane conversion and high selectivity to synthesis gas can be obtained either by increasing contact time or by raising reaction temperature. As shown in Fig. 3, both conversion and selectivity sharply increase as contact time increases from ca 1×10^{-3} to 6×10^{-3} s · g/ml. Conversion and selectivity close to those predicted by thermodynamic equilibrium are achieved at a contact time of approximately 6×10^{-3} s · g/ml. This contact time corresponds to a superficial contact time of 2×10^{-3} s. Figure 4 shows the O_2 and CH_4 conversions and CO selectivity, obtained at different temperatures over the Ni/La_2O_3 catalyst. The reaction was first initiated at 800°C. After reaching the stable performance, the reaction temperature was reduced stepwise. It is shown that the extent of reaction is negligibly small when temperature is below ca 550°C. As reaction temperature

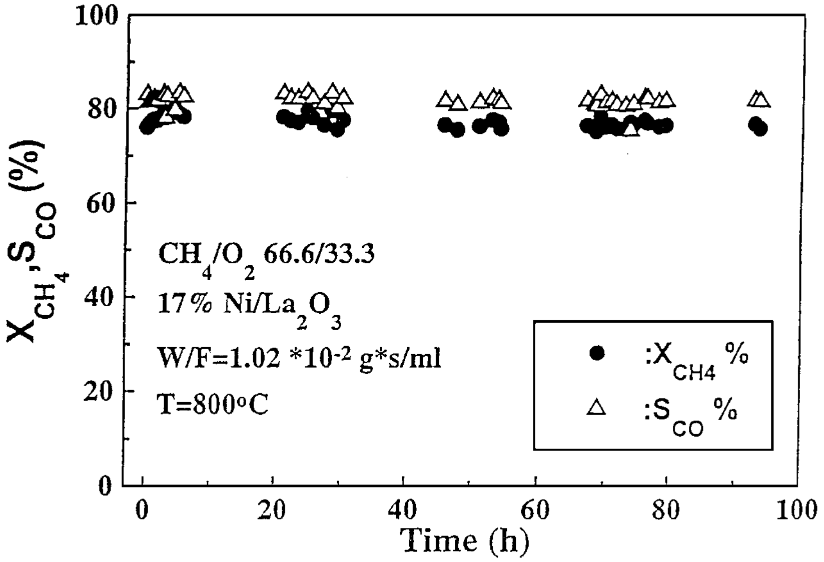

FIG. 2. Alteration of methane conversion and CO selectivity as a function of time on stream over a 17 wt% Ni/La_2O_3 catalyst at 800°C, using undiluted CH_4/O_2 mixture ($CH_4/O_2 = 2$).

increases from 550°C to ca 650°C, oxygen conversion increases rapidly, producing CO_2 as the major product. Further increase of the reaction temperature (>650°C) results in consumption of all the oxygen content ($X_{O_2} = 100\%$), and enhancement of methane conversion and CO selectivity. The formation of CO and further conversion of methane, after complete consumption of oxygen in the reaction mixture, should be attributed to the occurrence of reforming reactions on the reduced Ni surface.

The variation of CO selectivity with oxygen and methane conversion was studied at the temperature of 800°C. It was found that while oxygen was present in the reaction

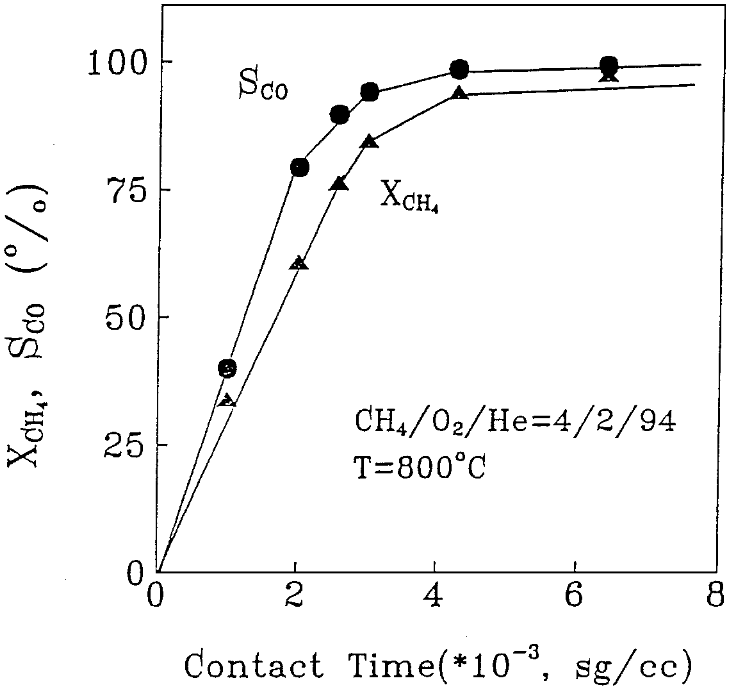

FIG. 3. Influence of reaction contact time on methane conversion and CO selectivity obtained over a 17 wt% Ni/La_2O_3 catalyst. $T = 800°C$, $CH_4/O_2/He = 4/2/94$ vol%.

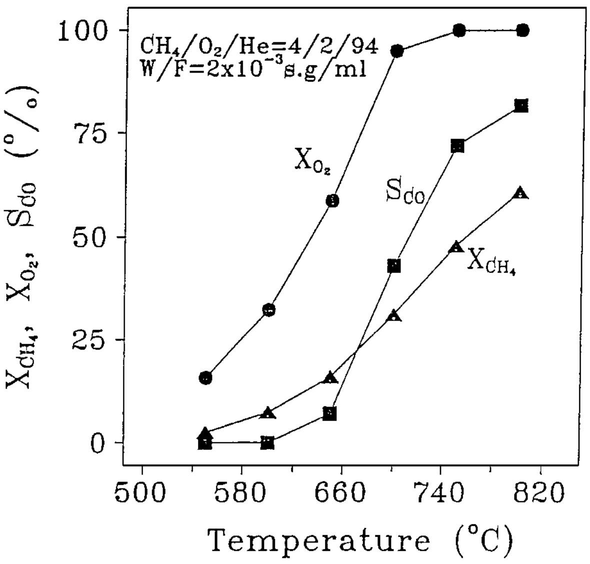

FIG. 4. Influence of reaction temperature on methane and oxygen conversion, and CO selectivity obtained over the 17 wt% Ni/La_2O_3 catalyst. $CH_4/O_2/He = 4/2/94$ vol%, $W/F = 2 \times 10^{-3}$ s · g/ml.

mixture ($X_{O_2} < 100\%$, $X_{CH_4} < 30\%$) selectivity towards CO formation was very low (<10%). Selectivity to CO increased rapidly at higher methane conversions due to CO_2 and steam reforming of methane on reduced Ni sites. This observation demonstrates that the catalytic partial oxidation of methane on Ni catalysts follows the indirect scheme, i.e. combustion of methane followed by CO_2 and steam reforming reactions of the unconverted methane.

The variation of the initial ($X_{CH_4} < 10\%$) selectivity for CO and CO_2 formation with the P_{CH_4}/P_{O_2} ratio, at a constant methane partial pressure of 1.32 KPa and a reaction temperature of 600°C is illustrated in Fig. 5a. It can be seen that CO selectivity is nearly 100% at high (>20) P_{CH_4}/P_{O_2} ratios. However, nearly zero selectivity towards CO formation is observed at low (<4) P_{CH_4}/P_{O_2} ratios, which are of practical interest. Initial selectivity towards CO formation at 600°C is also presented in Fig. 5b as a function of the P_{CH_4}/P_{O_2} ratio at constant oxygen partial pressures of 0.3 and 0.2 kPa. It is shown that at a P_{CH_4}/P_{O_2} ratio of 5, CO selectivity is zero at oxygen partial pressure of 0.3 kPa, while it is over 30% at oxygen partial pressure of 0.2 kPa. In order to achieve nonzero CO selectivities at the high oxygen partial pressure, the P_{CH_4}/P_{O_2} ratio must exceed the value of 7. Further increase of the P_{CH_4}/P_{O_2} ratio leads to further increase of CO selectivity which approaches 45% at P_{CH_4}/P_{O_2} ratio equal to 17. The results presented in Figs. 5a and b clearly demonstrate that the initial selectivity towards CO formation does not depend uniquely on the P_{CH_4}/P_{O_2} ratio but also on the partial pressure of oxygen in the reaction mixture. In fact it was found that for oxygen partial pressures exceeding 1 kPa selectivity towards CO formation was essentially zero, regardless of the P_{CH_4}/P_{O_2} ratio. This is probably related to the extent of oxidation of the Ni particles under reaction conditions. At low oxygen pressures, the Ni surface is reduced and CO is produced almost exclusively. As the oxygen pressure is increased, Ni is gradually oxidized and CO selectivity decreases. At oxygen pressures higher than approximately 1 kPa, oxidation of the Ni surface is apparently complete and the catalyst is active for methane combustion only. At the downstream part of the catalyst zone which is deficient in oxygen concentration and the P_{CH_4}/P_{O_2} ratio approaches high enough values, the production of CO via the direct route over the Ni/La_2O_3 catalyst might be significant.

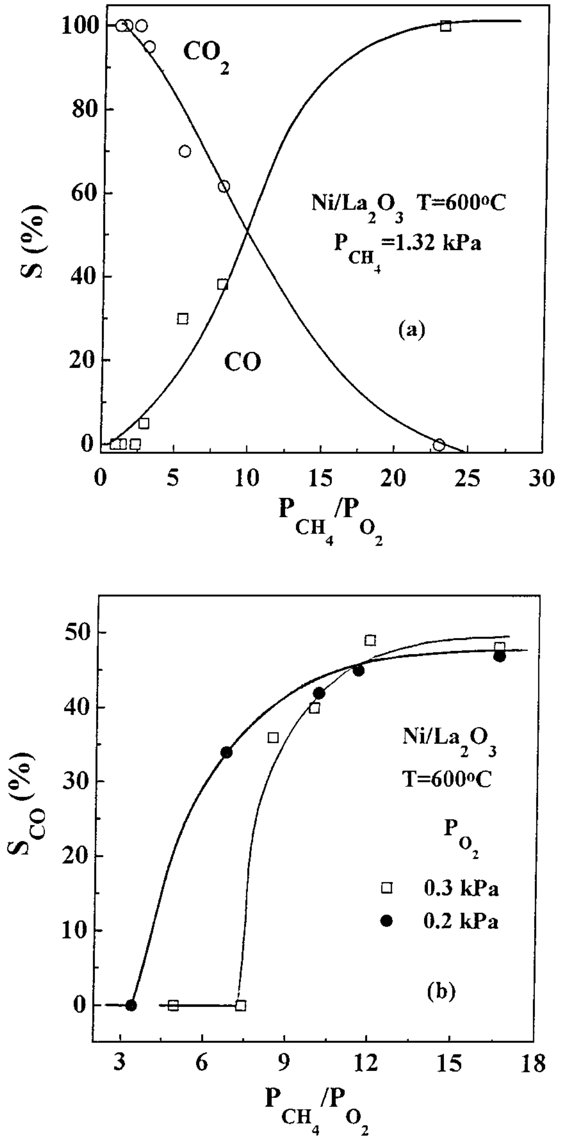

FIG. 5. (a) Alteration of CO and CO_2 selectivities with P_{CH_4}/P_{O_2} ratio during CPO reaction at 600°C and methane partial pressure equal to 1.32 kPa. (b) Alteration of CO selectivity with P_{CH_4}/P_{O_2} ratio during CPO reaction at 600°C and oxygen partial pressure equal to 0.3 and 0.2 kPa.

TABLE 1

Chemisorptive Parameters of 17 wt% Ni/La_2O_3 and 17 wt% Ni/Al_2O_3 Catalysts

Catalyst 17 wt% Ni/	Technique[a]	Reduction temperature °C	Uptake cm^3/g_{cat}	Dispersion %	Particle size Å
Al_2O_3	H_2 Chemisorption	750	0.99	3.0	330
	CO Chemisorption	750	1.97	3.1	323
	H_2 Desorption	750	1.27	3.8	263
La_2O_3	H_2 Chemisorption	750	0.33	1.0	1100
	CO Chemisorption	750	0.22	0.3	3240
	H_2 Desorption	750	0.42	1.3	846
	H_2 Desorption	300	0.39	1.2	917
	H_2 Desorption	750/300[b]	0.32	1.0	1134
	XRD[c]	750	—	—	330

[a] The chemisorption experiments were conducted at 25°C, while the desorption experiments (after chemisorption at 25°C) were carried out in the temperature range of 25–500°C.

[b] After reduction at 750°C for 2 h, the reduced catalyst was exposed to air overnight at room temperature and then reduced again in H_2 flow at 300°C for 10 h.

[c] The results were obtained employing Scherrer's equation.

Similar behavior was observed by Hu and Ruckenstein (5), who studied the kinetics of methane oxidation by the TAP technique. They reported that CO selectivity is dependent on the oxygen binding ability of the catalyst and on the state of the surface of Ni present in the catalyst.

3.3. *Catalyst Characterization*

Results of H_2 and CO chemisorption, at room temperature, on Ni/La_2O_3 and Ni/γ-Al_2O_3 catalysts are reported in Table 1. Before the measurement, the sample (which had already been reduced in H_2 flow at 500°C for 5 h) was further reduced at 750°C in H_2 atmosphere for 2 h. Based on the results of room-temperature H_2 chemisorption, nickel dispersions of 1 and 3% were found for the 17 mass% Ni supported on La_2O_3 and γ-Al_2O_3 carriers, respectively. The apparently low Ni dispersions (ca 3%) on the γ-Al_2O_3 carrier is mainly due to conversion of a large portion of metallic nickel to nickel aluminate, $NiAl_2O_4$, as shown by XRD (10, 19,23), which is incapable of chemisorbing H_2 or CO. The reason for the unusually low Ni dispersions (0.3–1%) on the La_2O_3 carrier is unclear. A previous XRD study conducted in this laboratory (19) showed that the Ni/La_2O_3 catalyst consists of metallic Ni and La_2O_3 phases only. Since the most prominent peak of Ni is well-separated from those of the carrier (which is not the case in Ni/Al_2O_3), it allows to estimate the Ni particle size by employing Scherrer's equation. It is estimated that the average particle size present on the La_2O_3 support is of the order of 330 Å. This value is much smaller than 1100 and 3240 Å deduced from H_2 and CO chemisorption, respectively (Table 1). Although different techniques may result in different metal particle sizes, the large difference in metal particle size, up to 3–10 times, cannot be simply attributed to uncertainties of the techniques, particularly for the present case where a high nickel metal loading (17 mass%) is used. It seems that H_2 and CO chemisorption on the Ni/La_2O_3 catalyst are significantly suppressed.

CO chemisorption on supported Ni catalysts has been extensively studied by FTIR, due to the high sensitivity of this technique to adsorbed CO species. It is well established that CO rapidly chemisorbs on metallic Ni sites to form linearly and bridged adsorbed CO species, and the frequencies of these bands lie between 1800–2100 cm^{-1}, depending on the nature of the carrier, Ni particle size, and chemisorption conditions (e.g. temperature and gas composition). In order to verify the deduction that H_2 and CO chemisorption on the Ni/La_2O_3 catalyst is suppressed, the surface species formed upon CO chemisorption on the Ni/La_2O_3 and Ni/γ-Al_2O_3 catalysts were investigated by FTIR. Figure 6 shows the FTIR spectra obtained on the Ni/La_2O_3 and Ni/γ-Al_2O_3 catalysts after exposure to 5% CO/Ar mixture. At least eight bands between 1150 and 2480 cm^{-1} are observed on the Ni/γ-Al_2O_3 catalyst. The bands at 2121 and 2184 cm^{-1} are due to gaseous CO. The bands at 1958 and 2055 cm^{-1} are assigned to the bridged and linearly adsorbed CO on Ni crystallites, respectively. The four bands at 1227, 1356, 1438, and 1651 cm^{-1} can be assigned to the formate and bicarbonate species, presumably on the γ-Al_2O_3 support. It is interesting to observe the gaseous CO_2 band at 2352 cm^{-1} upon exposure of the reduced Ni/γ-Al_2O_3 to CO at room temperature. This band was found to increase as the adsorption temperature was increased up to 400°C, while the formate and bicarbonate species were found to slightly decrease. The formation of CO_2 should be attributed to either decomposition of formate and bicarbonate species, which are not very stable over Al_2O_3 support at high temperatures, or CO disproportionation. Moreover, the bands corresponding to formate and bicarbonate species were found to easily decompose under O_2 or H_2 treatment at 400°C. Production of CO_2, at about 500°C, was also confirmed by mass spectrometer measurements, upon passing CO through a reactor which contained the reduced Ni/γ-Al_2O_3 catalyst, while the temperature was increased from 25°C to 625°C (23). This can be explained by the fact that the mobile CO species, after overcoming the activation energy barrier, can partly desorb into the gas phase and partly attack the neighboring oxygen adatoms to form CO_2. It is also possible that the CO which has already desorbed from the surface, readsorbs and reacts with the surface oxygen adatoms to produce CO_2. From the results of CO chemisorption (Table 1) and FTIR spectra (Fig. 6), it can be derived that the Ni/Al_2O_3 catalyst favors CO chemisorption and disproportionation to CO_2 and C, much more than the Ni/La_2O_3 does.

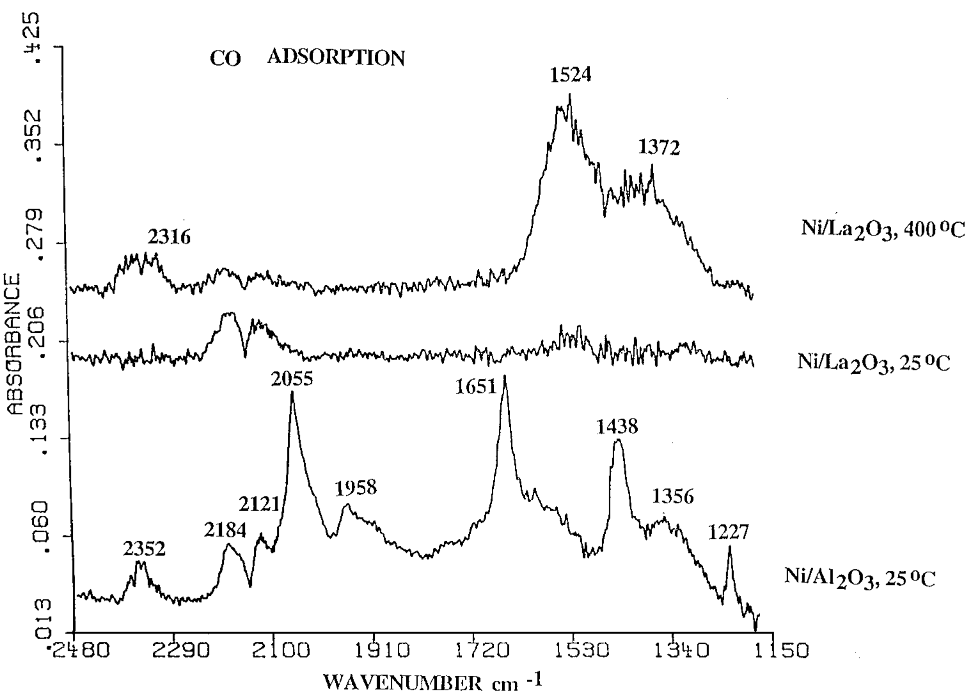

FIG. 6. FTIR spectra obtained upon exposure to 5% CO/Ar of (a) 17 wt% Ni/γ-Al_2O_3 at 25°C; (b) 17 wt% Ni/La_2O_3 at 25°C; and (c) 17 wt% Ni/La_2O_3 at 300°C.

Under CO chemisorption on the Ni/La_2O_3 catalyst at room temperature, only the two gaseous CO bands at 2121 and 2184 cm^{-1} are observed. A very weak band at around 1520 cm^{-1} may exist among the noisy background in the region between 1300 and 1600 cm^{-1}. When the temperature for CO chemisorption is elevated to 400°C, five bands at 1372, 1524, 2121, 2184, and 2316 cm^{-1} are observed. While the bands at 2121 and 2184, and 2316 cm^{-1} correspond to gaseous CO and CO_2, respectively, the two bands at 1372 and 1524 cm^{-1} are assigned to carbonate species on the La_2O_3 support, presumably due to the involvement of hydroxyl groups of the support. These species are quite stable as the intensity of the corresponding bands was found not to change following an Ar purge at 600°C for 30 min or following 30 min H_2 treatment, followed by 30 min O_2 treatment at 600°C. On the other hand, the same treatment applied to the Ni/Al_2O_3 catalyst after CO chemisorption was sufficient to fully decompose the formate species formed over the Al_2O_3 support. The small production of gaseous CO_2 which was observed can be mainly attributed to CO disproportionation ($2CO \rightarrow C + CO_2$) on the well-reduced Ni crystallites and to a smaller degree, since the sample is very dry, to the water–gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) occurring on the La_2O_3 support at the elevated chemisorption temperature. The surprising result is the failure to observe any adsorbed CO species on the Ni/La_2O_3 catalyst. The FTIR spectra shown in Fig. 6 confirm the results of equilibrium H_2 and CO chemisorption which show suppression of the chemisorptive capacity of the Ni/La_2O_3 catalyst (Table 1). These results imply that a large fraction of the Ni sites are not accessible to gaseous molecules.

The results of the present study, namely the enhanced stability of the Ni/La_2O_3 catalyst under conditions of partial oxidation of methane, can be explained taking the following facts into account: The observed reduction of activity with time on stream of conventional Ni-based catalysts in the process of partial oxidation of methane is most probably due to carbon accumulation in the latter part of the catalyst bed, where no oxygen is present and methane is being reformed by H_2O and CO_2. It has been shown in this laboratory that under conditions of dry reforming of methane (CH_4/CO_2) which cause the highest rate of carbon accumulation on Ni catalysts, the Ni/La_2O_3 catalyst is stable with time on stream. This phenomenon was shown to be due to decoration of the Ni particles by LaO_x species as well as oxycarbonate species which interact with carbon at the periphery of the Ni-LaO_x interfacial area, converting it to CO (21). Thus, a fraction of the Ni surface is continuously cleaned of carbon and continuously participates in the reaction. As long as the rate of carbon scavenging by LaO_x or oxycarbonate species is equal to the rate of carbon deposition, the catalyst exhibits a stable operation with time on stream.

The observed suppression of H_2 and CO chemisorption on the Ni/La_2O_3 catalysts (Table 1), by a factor of 3 to 10, based on metal dispersion estimated by XRD line broadening, can also be explained by the model according to which a portion of the Ni surface is covered by LaO_x species, originating from the La_2O_3 carrier, which prevent H_2 and CO adsorption. The fact that the suppression of H_2 and CO adsorption was observed on Ni/La_2O_3 samples which had not been exposed to reaction conditions implies that decoration of the Ni particles by species originating from the carrier occurs during the preparation of the catalysts. This was recently confirmed by high resolution TEM which clearly showed lanthanum-containing species to cover a portion of the surface of the Ni particles, primarily close to the carrier–metal interphase (25).

In order to further study the nature of the interaction between Ni and lanthanum species which are decorating the Ni crystallites and its possible relation to the SMSI phenomenon, the Ni/La_2O_3 catalyst was pretreated under different conditions and the H_2 uptake was subsequently measured. The H_2 chemisorption was performed at room temperature for 0.5 h, while the H_2 desorption was carried out under He flow as the temperature was increased from 25°C to 500°C, at the rate of 28°C/min. These experiments were conducted in an apparatus which allows performing different pretreatments and which is connected to a mass spectrometer for detection. The respective results are presented in Table 1. It is seen that the uptake of H_2 during H_2 adsorption on the Ni/La_2O_3 catalyst ranges from 0.32 to 0.42 cm^3/g_{cat}, being insensitive to the type of pretreatment. High Ni loadings permit to accurately measure the H_2 uptake. The H_2 uptake on the Ni/La_2O_3 catalysts after reduction at 750°C for 2 h is approximately the same as the one after reduction at 300°C for 10h, indicating that no SMSI state was induced after high temperature reduction. This is further supported by the observation that the H_2 uptake after reduction at 750°C for 2 h is approximately the same as the one after reduction at 750°C for 2 h, followed by exposure to air at room temperature overnight and then reduction again at 300°C for 10 h. Apparently, the decoration of the Ni crystallites by lanthanum species is not due to migration of lanthanum species onto Ni crystallites during high temperature reduction, as in the case of the SMSI phenomenon, which only occurs when the catalyst support is reducible and metal dispersion is high. It is highly possible that the decoration of the Ni crystallites by lanthanum species occurs during the procedure of catalyst preparation. La_2O_3 has a fairly high basicity, while the metallic Ni precursor, $Ni(NO_3)_2$, is of acidic nature. It can be reasonably inferred that during the impregnation step (at 110°C) a small amount of lanthanum species are dissolved in the aqueous solution and tend to associate with the nickel compound due to acid–base interaction. After decomposition of the nickel nitrate and reduction of the nickel oxide, the lanthanum species which are associated with the Ni compound remain on the surface of the Ni crystallites.

4. CONCLUSIONS

The following conclusions can be drawn from the results of the present study:

(1) The Ni/La_2O_3 catalyst is capable of exhibiting good activity and stability towards the partial oxidation of methane to synthesis gas, using the stoichiometric ratio of CH_4/O_2 (=2).

(2) Conversions and selectivities close to those predicted by thermodynamic equilibrium can be achieved at a contact time $\geq 6 \times 10^{-3}$ s · g/ml (at 800°C and with a reaction mixture of $CH_4/O_2/He = 4/2/94$ vol%).

(3) Kinetic results reveal that the partial oxidation of methane to synthesis gas over the Ni/La_2O_3 catalyst follows mainly the indirect reaction scheme; i.e., methane is first deeply oxidized to CO_2 and H_2O, and then the unconverted methane is reformed with CO_2 and H_2O to produce synthesis gas, while CO formation via the direct route is observed at low oxygen partial pressures and high P_{CH_4}/P_{O_2} ratios.

(4) CO chemisorption over Ni/La_2O_3 catalyst, studied by FTIR spectroscopy, has shown that only carbonate species are formed over La_2O_3 at elevated temperatures. These species are quite stable under He, H_2, and O_2 treatment at 600°C.

(5) Ni particles, dispersed on the La_2O_3 support, are fairly large (≥300 Å), while a portion of Ni crystallites is decorated by lanthanum-containing species. It is proposed that the enhanced stability of the Ni/La_2O_3 catalyst towards partial oxidation of methane to synthesis gas is related to the decoration of the Ni particles by LaO_x species, which favors the removal of excess carbon deposition on the Ni crystallites.

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