JOURNAL OF CATALYSIS **179,** 292–299 (1998)
ARTICLE NO. CA982183

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

II. Transient, FTIR, and XRD Measurements

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Received June 23, 1997; revised October 21, 1997; accepted October 29, 1997

Ni/La_2O_3 and Ni/Al_2O_3 catalysts were studied under conditions of partial oxidation of methane to synthesis gas. Temperature-programmed oxidation and hydrogenation experiments have shown that carbon accumulation over Ni/La_2O_3 during CPO remains essentially constant after 2 h time on-stream, while over Ni/Al_2O_3 it increases during the initial several hours. FTIR spectroscopy of surface species formed over the Ni/La_2O_3 catalyst under reaction conditions indicates that the carbonate species formed over the support do not decompose under He and O_2 treatment at 600°C. XRD spectra obtained following high ($\sim$90%) or low ($<$10%) methane conversions show that Ni, La_2O_3, $La_2O_2CO_3$, NiO, and Ni_3C phases are present in the case of high methane and complete oxygen conversions, while nickel oxide, nickel carbide and, to a small extent, $La_2O_2CO_3$ phases are present in the case of low CH_4 and incomplete oxygen conversions.

1. INTRODUCTION

The catalytic partial oxidation (CPO) of methane to synthesis gas over Ni/La_2O_3 and Ni/Al_2O_3 catalysts was discussed in the first part of this series (1). It was shown that the Ni/La_2O_3 catalyst exhibits good activity and unique stability with time on-stream, as compared to other Ni-based catalysts. The objective of the present study is to provide a mechanistic understanding of the differences between the Ni/La_2O_3 and Ni/Al_2O_3 catalysts which lead to significantly different catalytic performance.

Carbon deposition on catalysts during the partial oxidation of methane has been investigated by Claridge *et al.* (2), and it was found that the relative rate of carbon deposition follows the order $Ni > Pd > Rh > Ir$. Methane decomposition was found to be the principal route for carbon formation over a supported nickel catalyst, and electron micrographs 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.

In the present work, aspects of CPO of methane over Ni/La_2O_3 and Ni/Al_2O_3 catalysts are discussed. The Ni/La_2O_3 catalyst has also been investigated in our laboratory under conditions of CO_2 reforming of methane (3–5). It was shown that this catalyst, in contrast to other Ni-based catalysts, exhibits excellent stability with time on-stream. As it has been presented in part I of this study (1), the Ni/La_2O_3 catalyst exhibits excellent activity and stability towards CH_4/O_2 as well. The differences between the Ni/La_2O_3 and Ni/Al_2O_3 under CPO reaction conditions are investigated, employing transient, FTIR, and XRD techniques.

2. EXPERIMENTAL

2.1. *Catalyst Preparation*

The methods of preparation and characterization of the present Ni/La_2O_3 and $Ni/\gamma\text{-}Al_2O_3$ catalysts have been described in part I of this work (1).

2.2. *Transient Studies*

The flow apparatus and reactor used for the transient experiments has been described in a previous publication (6). Chemical analysis of the gases during transients was done by an on-line mass spectrometer (Fisons, SXP Elite 300H) equipped with a fast response inlet capillary system. In the multiple peak data acquisition mode, 4 peaks/s could be followed with good signal-to-noise ratio. Calibration of the mass spectrometer signal was performed based on prepared mixtures of known composition. Methane transients were recorded at m/e 15, while CO, CO_2, and H_2 transients at $m/e = 28$, 44, and 2, respectively. For the CO measurement in the presence of CO_2 the contribution of the CO_2 to the 28 peak was found to be such that the intensity ratio 28/44 for CO_2 was 0.12. The CH_4/O_2 mixture was prepared with the composition 4% CH_4, 2% O_2, and 94% He.

TPO and TPH (temperature-programmed oxidation and hydrogenation) experiments were performed as follows: a

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0021-9517/98 $25.00

stream of $CH_4/O_2/He = 4/2/94$ vol% was passed over the catalyst at the temperature range of 600–800°C, with flow rate sufficient to achieve methane conversions of 70–80% for a certain period of time. The feed was subsequently switched to He for 5 min at the reaction temperature, followed by cooling of the reactor to room temperature under He flow. The feed was then changed to pure H_2 or 5% O_2/He while, at the same time, the temperature was increased to 900°C at the rate of 35°C/min to carry out a TPH or TPO experiment. The reduction characteristics of Ni/La_2O_3 and Ni/Al_2O_3 catalysts were studied as follows: The freshly reduced catalyst sample was first treated with 10% O_2/He at 750°C for 1 h. The feed was then switched to He for 5 min at 750°C, and the reactor was subsequently cooled in He flow to 300°C. The feed was then switched to 1% H_2/He mixture, while the temperature was increased to 750°C at the rate of 30°C/min. The H_2 response was followed by on-line mass spectrometry.

2.3. Surface Species Studied by FTIR Spectroscopy

A Nicolet 740 FTIR spectrometer equipped with a diffuse reflectance cell was used for the measurement of surface species formed on the catalysts during CPO of methane. The cell, containing ZnSe windows which were cooled by water circulating through blocks in thermal contact with the windows, allowed collection of spectra over the temperature range of 25–700°C at atmospheric pressure. For all the spectra recorded, a 32-scan data accumulation was carried out at a resolution of 4.0 cm^{-1}. An IR spectrum obtained under Ar flow (before the reaction) was used as the background to which the spectra, after reaction, were ratioed. The sample used (~50 mg) was in finely powdered form and its surface was carefully flattened in order to increase the intensity of the IR beam by reflection. Before exposure to the reaction mixture, the catalyst sample was heated in Ar to 500°C and then the feed was changed to H_2 for 1 h for reduction.

2.4. XRD Analysis

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 under an inert atmosphere for measurements.

3. RESULTS AND DISCUSSION

3.1. Determination of Carbon Accumulated under Reaction Conditions by Transient Methods

Temperature-programmed oxidation (TPO) and hydrogenation (TPH) of carbon species deposited on the surface of the Ni/La_2O_3 and Ni/Al_2O_3 catalysts during CPO of methane were conducted in order to determine the variation of the quantity of accumulated carbon with time on-stream and reaction temperature, as well as its reactivity toward hydrogenation and oxidation.

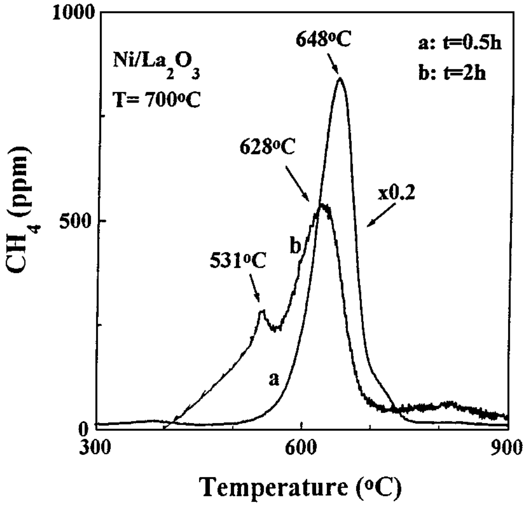

FIG. 1. Temperature-programmed hydrogenation of carbon species formed after (a) 0.5 h and (b) 2 h CPO reaction over Ni/La_2O_3 catalyst at 700°C.

Figure 1 presents the CH_4 responses during TPH conducted over Ni/La_2O_3, following CH_4/O_2/He reaction at 700°C for 0.5 h and 2 h. No higher hydrocarbons were detected during the TPH experiments. As is shown in Fig. 1, the majority of carbon is hydrogenated at temperatures higher than 500°C, while a small amount, corresponding to more active carbon, is hydrogenated at lower temperatures. It is also demonstrated that as time on-stream increases from 0.5 h to 2 h, the quantity of accumulated carbon decreases drastically from 0.23 to 0.03 mol C/mol Ni, while the temperature of the appearance of the CH_4 peak maximum decreases slightly, from 648°C to 628°C, which is probably due to the smaller amount of CH_4 formed in the second case. However, a smaller CH_4 peak is also observed at a lower temperature (531°C) and an even smaller one at 820°C hydrogenation temperature, in the 2-h reaction case.

The CO_2 responses obtained during TPO of carbon species accumulated over the Ni/La_2O_3 catalyst during CPO at 700°C for 0.5 h and 2 h are presented in Fig. 2. CO_2 is the only product of oxidation of carbon during TPO experiments. The quantity of carbon oxidized to CO_2 during TPO, as well as the temperature of the appearance of the CO_2 peak maximum, decreases with reaction time, exhibiting the same qualitative characteristics as during the TPH experiments. The quantity of carbon which is detected as CO_2 decreases from 0.19 to 0.02 mol C/mol Ni as time on-stream is increased from 0.5 to 2 h. Simultaneously, the temperature of the appearance of the CO_2 peak maximum is reduced from 775 to 696°C. Comparison of Figs. 1 and 2

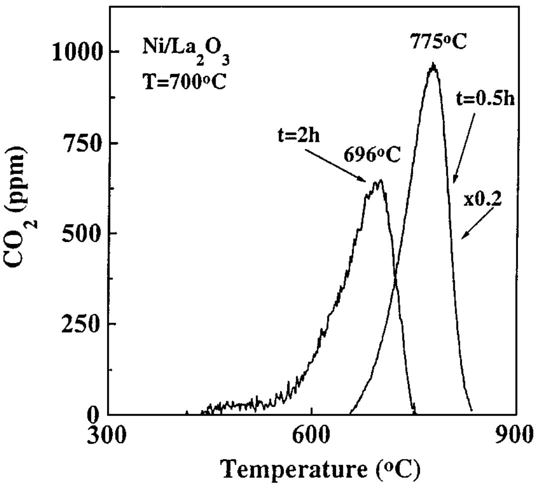

FIG. 2. Temperature-programmed oxidation of carbon species formed after 0.5 h or 2 h CPO reaction over Ni/La$_2$O$_3$ catalyst at 700°C.

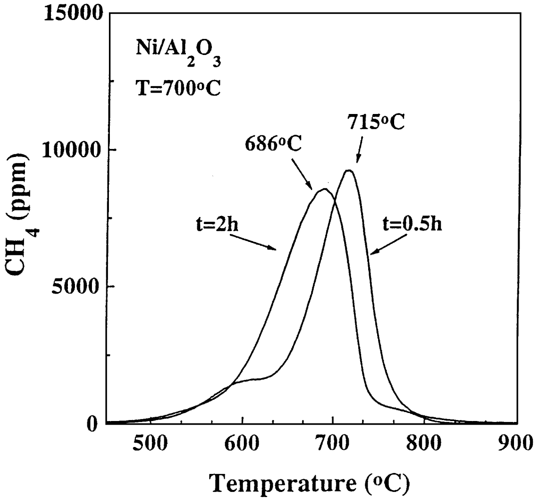

FIG. 3. Temperature-programmed hydrogenation of carbon species formed after 0.5 h or 2 h CPO reaction over Ni/Al$_2$O$_3$ catalyst at 700°C.

indicates that the quantity of carbon oxidized is much lower than that which is hydrogenated, while the CO$_2$ peak maximum appears at much higher temperatures than the respective CH$_4$ peak maximum. Thus, only a portion of the carbon accumulated during the CPO reaction over the Ni/La$_2$O$_3$ catalyst can be oxidized. It should also be stated that, since no chemical analysis was performed on the spent catalysts, it is not clear whether all accumulated carbon can be hydrogenated under the present conditions.

Experiments similar to those described with respect to Figs. 1 and 2 were conducted at different temperatures and for different periods of time-of-reaction. The main conclusion which derives from these experiments is that at all reaction temperatures the quantity of carbon increases as the reaction time increases from 15 min to 30 min; then it decreases as the reaction time increases up to 2 h and remains more or less stable as the reaction time increases further to 5 h. It was also found that in all cases, the quantity of carbon which is oxidized (TPO) is lower than that which is hydrogenated(TPH). However, it is worth mentioning that, although the quantity of carbon which is titrated with oxygen is only a portion of the total accumulated quantity, a negligible amount of CH$_4$ was produced during isothermal hydrogenation at 900°C, following a TPO procedure. Thus, oxidation of the accumulated carbon leads to stabilization of the remaining carbon species on the catalyst surface. These species must be the La$_2$O$_2$CO$_3$ species which are promoted with O$_2$ and decompose with H$_2$ at high enough temperatures. The formation of these species is the result of the interaction of the La$_2$O$_3$ support with CO$_2$ and CO products during reaction (4).

Figure 3 presents the CH$_4$ responses obtained during TPH experiments conducted over a Ni/Al$_2$O$_3$ catalyst after 0.5 and 2 h of CPO at 700°C. The quantity of carbon increases from 0.34 mol C/mol Ni to 1.08 mol C/mol Ni during this reaction time. The temperature of the appearance of the CH$_4$ peak maximum decreases from 715°C to 686°C as the reaction time increases from 0.5 h to 2 h. However, these temperatures are still higher than those obtained in the case of the Ni/La$_2$O$_3$ catalyst (Fig. 1), while the amount of titrated carbon is significantly larger, especially at the 2 h reaction time.

CO$_2$ responses during TPO of accumulated carbon over Ni/Al$_2$O$_3$ catalyst, after 0.5 and 2 h of CPO are presented in Fig. 4. The quantity of carbon detected by TPO on the catalyst surface after 2 h of reaction time is much higher than the respective one after 0.5 h of reaction. In addition, the carbon accumulated during 2 h of reaction seems to be more reactive than the one accumulated during 0.5 h of reaction. Comparison with the TPH experiments (Fig. 3)

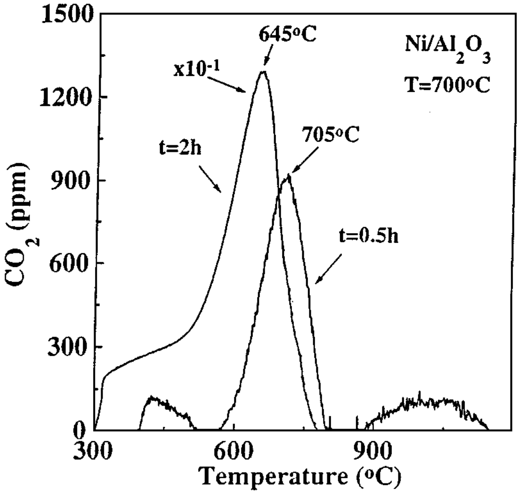

FIG. 4. Temperature-programmed oxidation of carbon species formed after 0.5 h or 2 h CPO reaction over Ni/Al$_2$O$_3$ catalyst at 700°C.

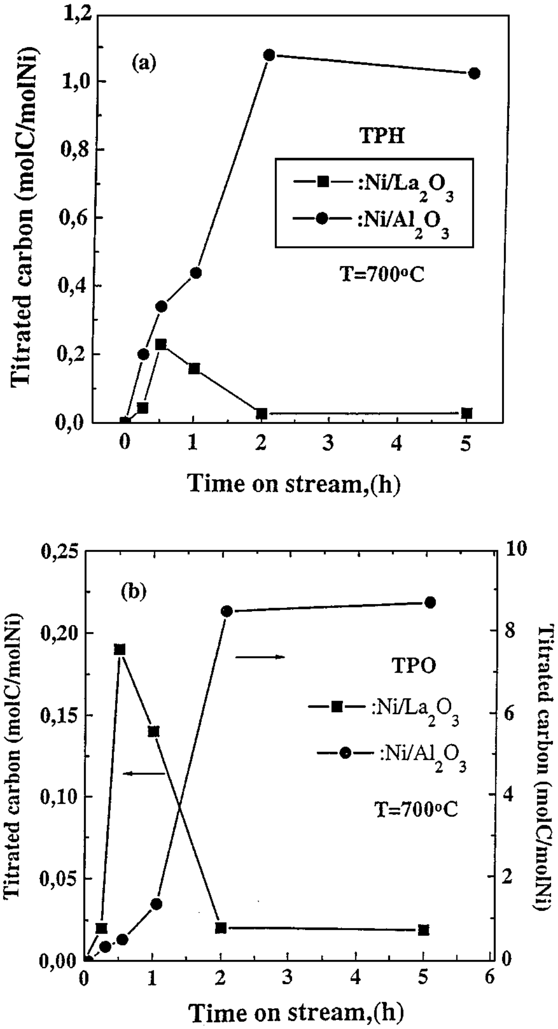

FIG. 5. Alteration of carbon formation with time of CPO reaction as detected by (a) TPH and (b) TPO experiments, with time on-stream, over Ni/La_2O_3 and Ni/Al_2O_3 catalysts at 700°C.

leads to the conclusion that the accumulated carbon over Ni/Al_2O_3 catalyst during CPO is hydrogenated at slightly higher temperatures than it is oxidized.

A comparison of the quantity of carbon detected by TPH as a function of time on-stream at 700°C over Ni/La_2O_3 and Ni/Al_2O_3 catalysts is presented in Fig. 5a. It is shown that the amount of carbon detected from the Ni/La_2O_3 catalyst after 5 h on stream is lower by more than one order of magnitude than the amount of carbon detected from the Ni/Al_2O_3 catalyst under identical conditions. In addition, the quantity of carbon detected over the Ni/Al_2O_3 catalyst after 2 h is five times greater than that observed after 15 min of CPO. In the case of Ni/La_2O_3, the quantity of carbon after 2 or 5 h seems to be approximately the same as that observed after 15 min of CPO reaction. A comparison of carbon deposited on Ni/La_2O_3 and Ni/Al_2O_3 catalysts during CPO reaction at 700°C, as detected by TPO is presented in Fig. 5b. The results derived from TPO experiments lead to the same conclusions with those derived from TPH experiments (Fig. 5a); i.e., the quantity of carbon accumulated over the Ni/Al_2O_3 catalyst increases significantly with time on-stream while over the Ni/La_2O_3 catalyst does not. Considering the fact that Ni/La_2O_3 catalyzes the indirect CPO route, i.e. combustion of CH_4, followed by reforming the remaining CH_4 with CO_2 and H_2O formed primarily, the good stability of this catalyst during CPO may be related to the stability observed during CO_2 reforming. Indeed, TPH, TPO, and isothermal experiments performed over the Ni/La_2O_3 catalyst under conditions of CO_2 reforming of CH_4 reveal that the carbon is more easily hydrogenated than oxidized and the accumulated quantity is stabilized at lower values after 5 h of reaction. These characteristics of the accumulated carbon over Ni/La_2O_3 under CO_2 reforming seem to be similar to those observed under CPO of methane.

The transient results for the detection of the quantity of accumulated carbon over Ni/La_2O_3 and Ni/Al_2O_3 catalysts are in good agreement with the kinetic results (1) which show excellent stability and high activity of the Ni/La_2O_3 and continuous deactivation of the Ni/Al_2O_3 catalysts. The continuous deactivation of Ni/Al_2O_3 is related to the increase of accumulated carbon with time on stream during the first hours of CPO.

The relative performance of Ni/Al_2O_3 as compared to Ni/La_2O_3 catalyst could also be related to the increased resistance of the former catalyst to be reduced, relative to that of the latter. The reduction characteristics of the two catalysts are shown in Fig. 6. As the H_2/He mixture is introduced over the catalyst at 300°C, a sharp increase in the H_2 response signal from its background value (under He

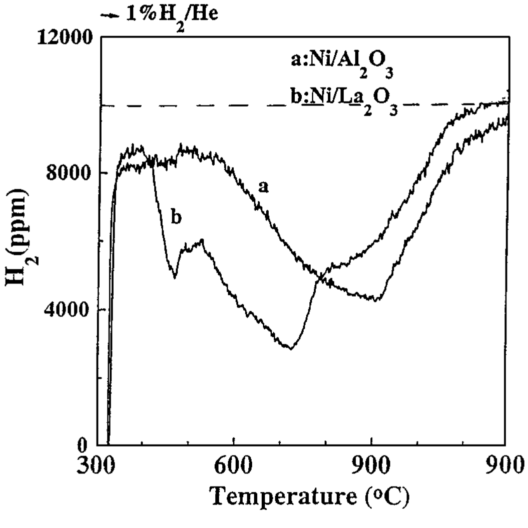

FIG. 6. Hydrogen responses observed during temperature-programmed surface hydrogenation of (a) Ni/Al_2O_3 and (b) Ni/La_2O_3 catalysts after their oxidation at 750°C for 1 h with 5% O_2/He mixture.

flow) toward the value corresponding to the feed concentration (1 mol%), is observed. However, as the temperature increases, the H_2 gas-phase concentration decreases, indicating that the catalysts are gradually reduced. The area between the dotted line (which corresponds to the feed composition) and the H_2 response curve designates the quantity of H_2 consumed. The consumption of H_2, which corresponds to the degree of reduction of the Ni crystallites, in the temperature range of 300–600°C is much higher in the case of Ni/La_2O_3 than in the case of Ni/Al_2O_3 catalyst. The H_2 response starts to increase as the temperature reaches 720°C for the Ni/La_2O_3 catalyst or 900°C for Ni/Al_2O_3. It is apparent that the reduction of NiO to Ni^0 occurs at a much lower temperature in the case of Ni/La_2O_3 than in the case of Ni/Al_2O_3 catalyst. Thus, considering the fact that the rate of reaction is directly related to the state of the Ni particles, the above observation for the reduction characteristics of the Ni/La_2O_3 and Ni/Al_2O_3 catalysts are of significance. Therefore, the higher activity and stable performance of Ni/La_2O_3 (1) may be related to the higher reducibility of Ni/La_2O_3. The higher resistance of Ni/Al_2O_3 catalyst toward reduction may control the performance of this catalyst during partial oxidation of methane, leading to the continuous deactivation with time on-stream, as the Ni particles are gradually oxidized or transformed to nickel aluminate and cannot be reduced under the reaction conditions.

3.2. FTIR Spectroscopy of Surface Species Formed during CPO of CH_4 over Ni/La_2O_3 Catalyst

The surface species formed upon exposure of the freshly reduced Ni/La_2O_3 catalyst to the reaction mixture consisting of $CH_4/O_2/Ar$ (=3.6/1.8/94.6 vol%) at 700°C for 10 and 30 min were investigated. It was found that two well-resolved IR bands, at 1548 and 1379 cm^{-1}, could be detected after 10 min of reaction at 700°C, as shown by curve a in Fig. 7. The intensity of these bands, which correspond to the formation of carbonate species on the La_2O_3 support during the CPO reaction, was found to increase with time of reaction, up to 30 min (Fig. 7b). However, a small shift of the wavenumbers at which the two peaks are detected was observed. These species were found to be stable following a 15-min purge with Ar, followed by a 30-min purge with 2% O_2/Ar at 700°C (Fig. 7c). It is interesting to note that no linear or bridged CO adsorbed bands were observed over Ni crystallites during the $CH_4/O_2/Ar$ reaction at 700°C. The carbonate species observed over Ni/La_2O_3 under reaction conditions can be attributed to the interaction of the La_2O_3 support with either CO or CO_2 reaction products. Indeed, the spectra presented in Fig. 7 compare well with spectra recorded during CO chemisorption over Ni/La_2O_3 at 400°C (1).

Figure 8 shows FTIR spectra observed over Ni/La_2O_3 catalyst after exposure to 5% CO_2/He in the temperature range of 25–700°C. Two well-resolved bands can be detected at 1570 and 1350 cm^{-1} which correspond to carbonate species over the La_2O_3 support. These bands increase as the reaction temperature increases from room temperature to 700°C. Curve f of Fig. 8 presents the spectra obtained after 30 min of Ar purge, followed by 30 min of 2% H_2/Ar exposure and 30 min of 2% O_2/Ar treatment at 700°C. It is apparent that the carbonate species do not seem to be affected by exposure to either H_2 or O_2 at the temperature of 700°C.

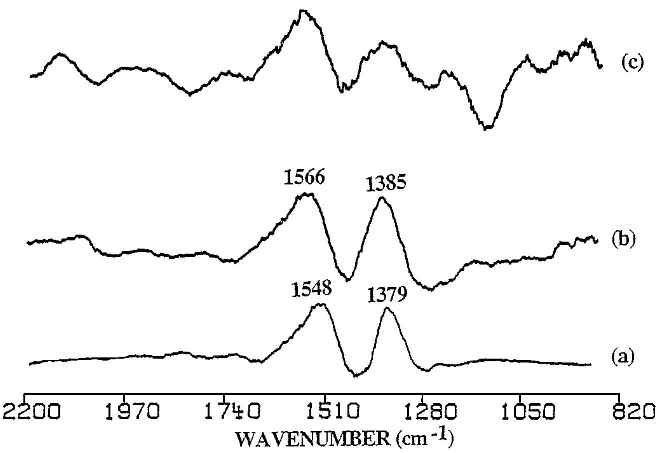

FIG. 7. FTIR spectra obtained after exposure of the Ni/La_2O_3 catalyst to $CH_4/O_2/Ar$ mixture at 700°C for 10 min (curve a) and 30 min (curve b) and after Ar purge at 700°C for 15 min, followed by a 30 min purge with 2% O_2/Ar at 700°C (curve c).

In contrast to this behavior, it is known that formate and carbonate species which are formed over Al_2O_3 support upon interaction with CO_2 or CO, decompose under He flow at high temperatures (up to 650°C) to give

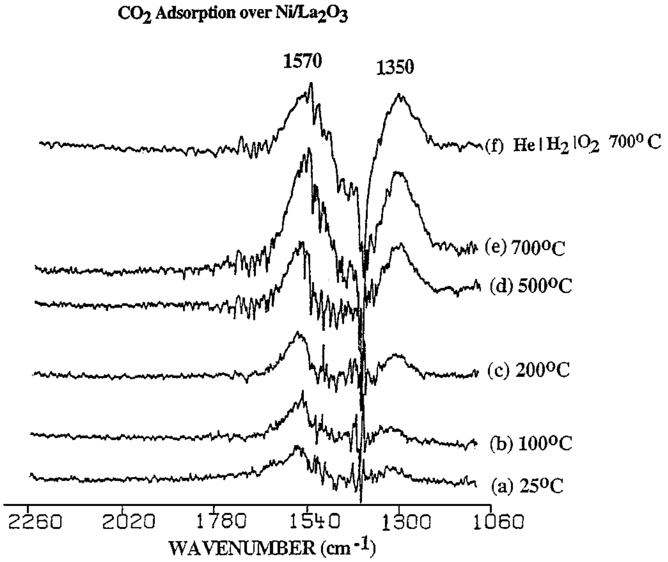

FIG. 8. FTIR spectra obtained after exposure of Ni/La_2O_3 catalyst to 5% CO_2/Ar mixture at (a) 25°C, (b) 100°C, (c) 200°C, (d) 500°C, (e) 700°C, and (f) after $Ar/H_2/O_2$ treatment at 700°C.

mainly CO_2 and H_2 (7, 8). The stability of the carbonate and formate species over Al_2O_3 was studied in this laboratory by exposure to 2% H_2/Ar mixture, while FTIR spectra were recorded at 200, 300, 400, and 500°C following a 10 min treatment with 2% H_2/Ar at each temperature (8). It was found that formate and carbonate species disappear in the temperature range of 400–500°C upon H_2/Ar treatment. In addition, the carbonate and formate bands formed over Al_2O_3 during exposure of the Ni/Al_2O_3 catalyst to CH_4/O_2/Ar, 5% CO/Ar, and 5% CO_2/Ar, were found to decompose under 2% H_2/Ar or 2% O_2/Ar treatment at temperatures up to 600°C. Thus, the stability of the carbonate and formate species on the La_2O_3 carrier is significantly higher than that over Al_2O_3. This is probably related to the much higher stability of the Ni/La_2O_3 catalyst (1) since, based on the mechanism of the reforming reactions which has been proposed (3, 9), these species are responsible for scavenging the carbon which is deposited on Ni from methane cracking, thus restoring the Ni surface to its original state.

At this point, it should also be mentioned that the quantity of carbon detected over the Ni/Al_2O_3 catalyst by TPH or TPO correspond to the real quantity of accumulated carbon on the nickel particles and not on the Al_2O_3 support. This is because the catalyst, before any titration of accumulated carbon, was exposed to He flow for 10 min at the reaction temperature (600–800°C), thus causing decomposition of the carbonate and/or formate species from the Al_2O_3 support. In the case of Ni/La_2O_3, some contribution to the CH_4 or CO_2 signals from decomposition of carbonate species cannot be excluded. This implies that the quantity of accumulated carbon (Figs. 1–4 and Table 1) might be overestimated.

FTIR has also been applied to study the species formed upon exposure of the Ni/La_2O_3 catalyst to CH_4/Ar at 700°C. No adsorbed bands were detected during the CH_4/Ar exposure of the catalyst surface, indicating that the adsorption of CH_4 onto the Ni/La_2O_3 catalyst is very weak.

3.3. *XRD Study of the Crystalline Phases Formed on Ni/La_2O_3 and Ni/Al_2O_3 Catalysts*

XRD was conducted in order to study the major crystalline phases of the Ni/La_2O_3 and Ni/Al_2O_3 catalysts under CPO reaction conditions. The catalysts which had been well reduced or exposed to the reaction mixture (CH_4/O_2/He ≈4/2/94) for 2 h, were quickly transferred to the XRD apparatus. Figure 9 shows the XRD spectra obtained over Ni/La_2O_3 and Ni/Al_2O_3 catalysts. In Fig. 9 curve a presents the crystalline phases observed over a fresh sample of Ni/La_2O_3 catalyst, curve b presents the crystalline phases observed after 2 h CPO reaction at 700°C under high methane and complete oxygen conversions, while curve c presents the crystalline phases observed after 2-h CPO reaction at 600°C under low methane conversions (≈10%) and O_2 conversion lower than 100% over the Ni/La_2O_3 catalyst. Metallic Ni and La_2O_3 phases can be detected over the fresh sample of Ni/La_2O_3 catalyst (curve a), while $La_2O_2CO_3$ and NiO phases are produced during reaction (curves b and c). The metallic Ni and La_2O_3 phases are present during reaction only in the case of high CH_4 conversions (curve b). The difference between the two spectra observed over the Ni/La_2O_3 catalyst, which had been exposed to different reaction conditions, can also be focused on the intensity of the crystalline phases. The intensity of the $La_2O_2CO_3$ phases, which is the product of the interaction of CO_2 or CO with La_2O_3, is lower in the case of low methane conversion (curve a) due to the low CO and CO_2 production. However, the existence of the metallic Ni phase during reaction leads to the suggestion that this is the active phase, responsible for the high activity and excellent stability observed over the Ni/La_2O_3 catalyst under CPO reaction conditions.

Ni-C phases can be observed during CPO reaction over Ni/La_2O_3 catalyst, due to carbon deposition originating from methane cracking. At least two Ni-C bands can be detected in the XRD spectra (curves b and c). One is due to the Ni_3-C phase and the other is due to the Ni-CO_3 phase. However, the existence of at least three kinds of carbon deposited on the Ni/La_2O_3 catalyst during the CPO reaction was observed by TPH (Fig. 1) and isothermal hydrogenation (not shown) experiments. Thus, the three different transient CH_4 peaks observed during hydrogenation experiments can be attributed to the Ni_3-C, Ni-CO_3, and $La_2O_2CO_3$ phases, which exist over the Ni/La_2O_3 catalyst during the CPO of methane reaction.

The crystalline phases observed over the Ni/Al_2O_3 catalyst as a fresh sample (curve d) and under high (∼90%)

TABLE 1

Effect of Reaction Time and Temperature on the Quantity of Accumulated Carbon (mol C/mol Ni), during CPO over Ni/La_2O_3 Catalyst, as Detected by TPH and TPO Experiments

Time (min)	15		30		60		120		300	
T(°C)	TPH	TPO	TPH	TPO	TPH	TPO	TPH	TPO	TPH	TPO
600	0.02	0.01	0.03	0.02	0.02	0.01	0.01	0.01	0.02	0.01
700	0.04	0.02	0.23	0.19	0.16	0.04	0.03	0.02	0.04	0.02
800	0.13	0.05	0.27	0.07	0.15	0.04	0.07	0.02	0.07	0.02

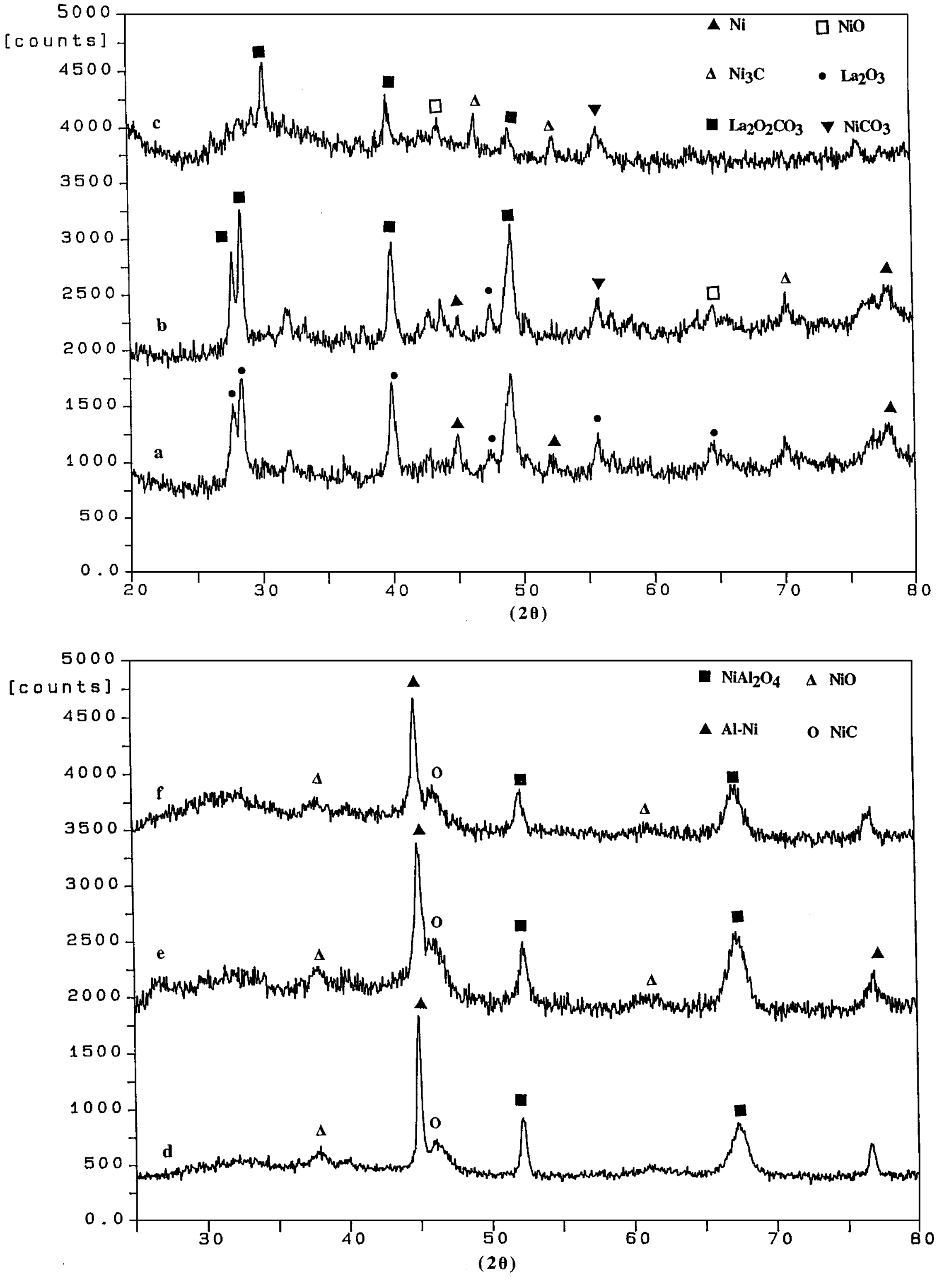

FIG. 9. XRD spectra obtained over fresh and used catalysts. Curve (a), freshly reduced Ni/La_2O_3; curve (b), Ni/La_2O_3 exposed to CPO at 750°C with high methane and complete oxygen conversions; curve (c), Ni/La_2O_3 exposed to CPO at 600°C with low methane and incomplete oxygen conversions; curve (d), freshly reduced Ni/Al_2O_3; curve (e), Ni/Al_2O_3 exposed to CPO at 750°C with high methane and complete oxygen conversions; curve (f), Ni/Al_2O_3 exposed to CPO at 600°C with low methane and incomplete oxygen conversions.

(curve e) and low (<10%) methane conversion (curve f) during CPO reaction, are also presented in Fig. 9. It is shown that very well resolved peaks corresponding to $NiAl_2O_4$ phases are present in all cases. In addition to the $NiAl_2O_4$ phase, nickel oxide (NiO) and nickel carbide (Ni_3C) are the only phases which exist during the CPO reaction over a Ni/Al_2O_3 catalyst. No metallic Ni could be detected even in the fresh sample, a result which is also confirmed by the XRD study performed by Zhang *et al.* (4).

Figure 9 clearly demonstrates the differences in the crystalline phases which exist in the reduced Ni/La_2O_3 and Ni/Al_2O_3 catalysts as well as after exposure to the identical reaction condition. In the case of Ni/La_2O_3, while metallic Ni is present on the reduced sample and on the one which had been exposed to reaction conditions corresponding to high methane conversion, no metallic Ni could be detected in the respective samples of the Ni/Al_2O_3 catalyst. The most dominant phase detected on Ni/Al_2O_3 was the $NiAl_2O_4$ phase, which, as has been reported in previous sections, exhibits high resistance to reduction, while it is incapable of chemisorbing CO or H_2. In addition to the $NiAl_2O_4$ phase, NiO and Ni_3C phases are formed during the CPO reaction. Thus the continuous deactivation of Ni/Al_2O_3 catalysts under CPO conditions is related to the existence of the $NiAl_2O_4$ phase, the oxidized nickel and carbon deposited on the Ni particles.

5. SUMMARY AND CONCLUSIONS

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

(1) Carbon accumulation during CPO over Ni/La_2O_3 is significantly less than that observed over Ni/Al_2O_3. The quantity of carbon accumulated over Ni/La_2O_3 decreases during the initial hours of reaction while it increases over the Ni/Al_2O_3 catalyst.

(2) The carbon accumulated during CPO is more reactive towards hydrogenation than oxidation in the case of a Ni/La_2O_3 catalyst, while the opposite trend is observed in the case of Ni/Al_2O_3. This observation is related to the capability of the carbonate species formed over Al_2O_3 to decompose under H_2 or O_2 treatment at 600°C, and the stability of the carbonate species formed over La_2O_3.

(3) The deactivation characteristics of the Ni/Al_2O_3 catalyst can be attributed to: (a) the higher quantity of carbon accumulated during CPO reaction, as compared to that observed over Ni/La_2O_3 catalyst; (b) the higher resistance of Ni/Al_2O_3 to be reduced as compared to that of Ni/La_2O_3, mainly due to the existence of $NiAl_2O_4$ phase; (c) the oxidized state of Ni particles even under conditions of complete oxygen conversion.

(4) FTIR spectra indicate that, during CH_4/O_2 reaction over Ni/La_2O_3 catalyst, carbonate species are formed due to the interaction of La_2O_3 with CO and CO_2 products. These species are rather stable when exposed to Ar, followed by H_2, followed by O_2 treatment at temperatures up to 700°C for 30 min.

(5) XRD analysis of the Ni/La_2O_3 catalyst which had been exposed to CPO reaction conditions has shown that the metallic Ni and the $La_2O_2CO_3$ phases are the active phases which promote catalyst stability. Transient and XRD results obtained over Ni/La_2O_3 catalyst reveal that three different kinds of carbon species are deposited during CPO reaction. These carbon species are in the form of Ni_3-C, Ni-CO_3, and $La_2O_2CO_3$.

ACKNOWLEDGMENTS

Financial support by the Commission of the European Union (Contract JOU2-CT92-0073) is gratefully acknowledged.

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