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Catalytic Reduction of NO by CO over Rhodium Catalysts

2. Effect of Oxygen on the Nature, Population, and Reactivity of Surface Species Formed under Reaction Conditions

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The effect of oxygen on the nature, population, and reactivity of surface species formed during reduction of NO by CO over Rh/TiO_2 catalysts has been examined employing FTIR and transient MS techniques. It has been found that the activity of Rh is hindered by accumulation of surface oxygen originating from NO decomposition and gas-phase oxygen in the feed. Adsorbed CO and reduced TiO_{2-x} species in the vicinity of Rh particles act as oxygen atom scavengers and, under fuel-rich conditions, remove atomic oxygen from the surface and restore the catalytic properties. Results of the present study provide additional evidence that production of N_2 is related to dissociation of adsorbed Rh–NO^- while production of N_2O is related to the presence of $Rh(NO)_2$. The presence of reduced Rh^0 sites is necessary for the formation of both reduction products. In the absence of oxygen in the feed, surface isocyanate species are also observed under reaction conditions. Their formation requires the presence of adjacent Rh^0–CO and reduced Rh^0 sites. Although these species are favored under conditions in which NO conversion to reduction products is observed, there is no evidence that they are catalytically active species.

Key Words: **NO; reduction of rhodium; titania catalyst; carrier carbon monoxide; FTIR;** *in situ* **transient (dynamic) reactivity.**

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1. INTRODUCTION

Catalytic removal of NO, originating from stationary and mobile sources, has been the subject of extensive investigation in recent years due to its importance for environmental protection (1). Concerning mobile sources, catalytic reduction of NO with CO over Rh catalysts is one of the most important reactions occurring in automotive catalytic converters, where both reactants are undesirable pollutants. However, the reaction is strongly inhibited by oxygen, thus making the catalyst insufficient for lean burn applications (2, 3).

CO and NO exhibit very well assigned infrared bands; therefore, IR spectroscopy has been frequently used to investigate the NO–CO reaction mechanism over a variety of catalysts, including Rh single crystals (4, 5) and Rh dispersed on carriers such as Al_2O_3 (6–12) and SiO_2 (13–17). In the first paper of this series (18) the adsorption and displacement characteristics of NO and CO were examined at 250°C over Rh catalysts supported on undoped and W^{6+}-doped TiO_2, employing FTIR and transient MS techniques. It has been found that four kinds of nitrogen oxide species may coexist in the adsorbed mode, namely Rh–NO^-(high), Rh–NO^-(low), $Rh(NO)_2$, and Rh–NO^+. Production of N_2 and N_2O in the gas phase involves the negatively charged and dinitrosyl species, respectively, while the positively charged species is inactive. In the present study, the formation and reactivity of surface species present under NO–CO reaction conditions as well as the effect of oxygen on their nature and population are examined over Rh/TiO_2 catalysts, employing FTIR and transient MS techniques.

2. EXPERIMENTAL

2.1. *Catalyst Preparation and Characterization*

The 0.5 wt% Rh/TiO_2 catalyst used in this study was prepared by the incipient wetness impregnation method using $RhCl_3 \cdot 3H_2O$ (Alfa) as metal precursor, following a procedure described elsewhere (18, 19). The dried material was then ground, sieved, and finally treated with H_2 at 300°C for 2 h. Metal dispersion of the catalyst was obtained by selective chemisorption of H_2 at 25°C, and was found to be 70% (34 μmol of Rh_s/g_{cat}) (18).

2.2. *Catalytic Performance Tests*

The apparatus used for the catalytic performance tests consists of a quartz reactor, a flow system, and an analysis system. The catalyst is placed in the reactor cell (7.0 mm i.d.) and secured by means of quartz wool. Temperature is measured in the middle of the catalyst bed by means of

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a K-type thermocouple. The flow system is equipped with four mass-flow controllers and a pressure indicator, which enables measurement of the pressure drop in the catalyst bed. Reaction gases (1.0% NO/He, 1.0% CO/He, 20.1% O_2/He, and He) are supplied from high-pressure gas cylinders and are of ultrahigh purity. The analysis system consists of an NO_x analyzer which enables continuous monitoring of NO and NO_2 concentration, and a gas chromatograph equipped with a TCD detector and two packed columns (molecular sieve 5A and Porapak Q) to separate and measure the concentration of O_2, N_2, N_2O, CO, and CO_2 at the effluent of the reactor. The reactor feed is analyzed in the same manner by bypassing the reactor.

The NO reduction experiments were performed using 50 mg of 0.5% Rh/TiO_2 catalyst, in the temperature range of 100 to 500°C, at atmospheric pressure. The feed composition was 1% O_2 (when used), 0.25% NO, and 0.5% CO (balance He). The total feed flow rate was 150 cm^3/min (W/F = 0.02 g s/cm^3). Preliminary experiments confirmed that, under the present conditions, there is no influence of external and internal mass transfer limitations on catalytic activity. Prior to reaction, the reduced catalyst was conditioned by *in situ* heating with He at 550°C for 1 h.

2.3. *FTIR and Transient MS Experiments*

FTIR spectra were obtained using a Nicolet 740 FTIR spectrometer equipped with a TGS detector and a KBr beam splitter. Infrared spectra of adsorbed species were obtained with a 32-scan data acquisition at a resolution of 4 cm^{-1} in a controlled gas atmosphere and temperature provided by a DRIFT cell. Details for the apparatus and procedures have been described in detail elsewhere (18). The transient MS experiments were carried out at 250°C by switching the feed composition to the reactor with the use of chromatographic valves equipped with electronic actuators. Since the principal peaks of CO and N_2 ($m/z = 28$) and CO_2 and N_2O ($m/z = 44$) cannot be separated, isotopic ^{15}NO was used in all transient MS experiments reported here. However, for reasons of simplicity, the mass number of isotopic ^{15}NO will not be indicated in the following. Further details are provided elsewhere (18).

3. RESULTS

3.1. *Catalytic Performance of Rh/TiO_2*

Results obtained on the performance of 0.5% Rh/TiO_2 catalyst for the selective catalytic reduction of NO by CO, in the absence and presence of oxygen, are shown in Figs. 1A and 1B, respectively. Catalytic performance is expressed in terms of steady-state conversions of NO and CO and in terms of yields of N_2O and N_2, as functions of the reaction temperature. At each temperature examined, a steady state was obtained before advancing to the next reaction temperature.

In the absence of oxygen in the feed, NO reduction by CO takes place above 150°C (Fig. 1A). Conversion of NO continuously increases with increasing reaction temperature and reaches 100% at temperatures above 300°C. In the temperature range of 150–300°C, the catalyst is highly selective toward N_2O formation, the yield of which goes through a sharp maximum at ca. 290°C and then drops to zero at temperatures above 350°C. The yield of N_2 continuously increases with increasing reaction temperature and reaches 100% above ca. 350°C (Fig. 1A). When 1% O_2 is added to the feed (Fig. 1B), the oxidation of CO reaches completion at 250°C. Reduction of NO is largely suppressed

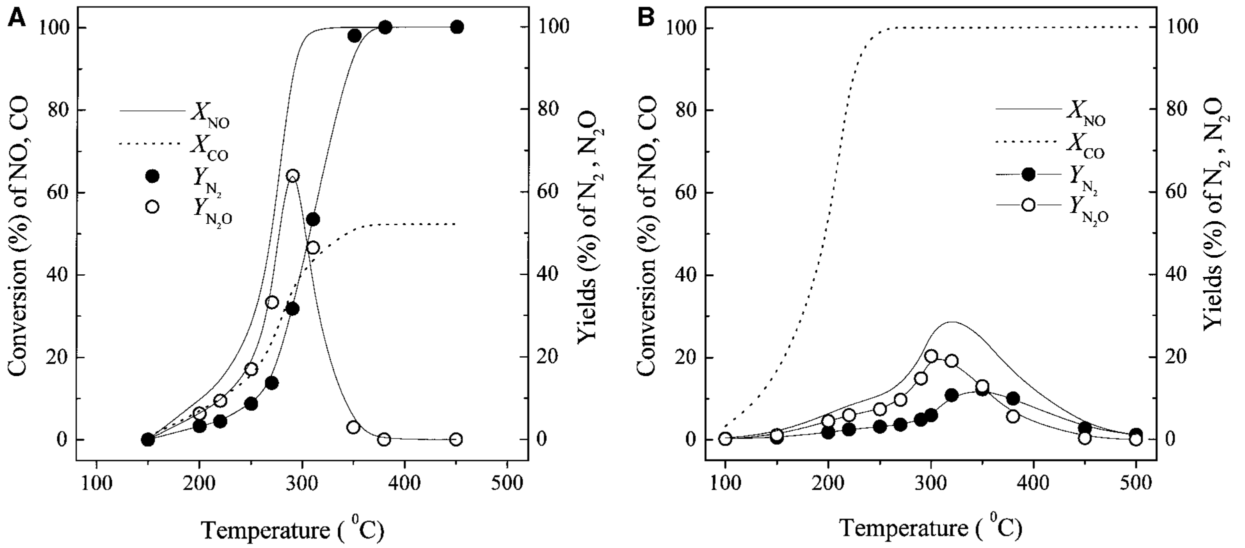


FIG. 1. Conversions of NO and CO, and yields of N_2 and N_2O as functions of reaction temperature in the absence (A) and presence (B) of oxygen. Feed compositions: (A) 0.25% NO, O.5% CO, (B) 0.25% NO, 0.5% CO, 1% O_2; W/F = 0.02 g s/cm^3.

by the presence of oxygen and its conversion goes through a maximum of ca. 30% at 320°C. Below this temperature, the catalyst is more selective toward N_2O, while above 350°C N_2 formation is favored (Fig. 1B).

3.2. FTIR Study of the Temperature-Programmed NO–CO Reaction

The nature and relative population of the surface species formed under reaction conditions, in the presence and absence of O_2, have been examined employing FTIR spectroscopy, as follows. The reduced catalyst was first exposed to the reaction mixture at room temperature (RT) and FTIR spectra were obtained as a function of time on stream until steady-state conditions were reached. Temperature was then stepwise increased and spectra were obtained 10 min after the desired reaction temperature was reached. Results obtained in the absence and presence of oxygen in the feed are presented in Figs. 2A and 2B, respectively.

In the absence of oxygen in the feed, interaction of Rh/TiO_2 with the reaction mixture at RT produces several IR bands in the 2250–1100 cm^{-1} region (Fig. 2A). Immediately upon exposure, the spectrum is dominated by bands at 2094, 2048, and 2027 cm^{-1}, which are in the ν(C–O) stretching frequency region. The band at 2048 cm^{-1} may be safely attributed to linearly bonded CO on reduced rhodium sites (Rh^0–CO) (20, 21). The bands located at ca. 2094 and 2027 cm^{-1} are assigned to the symmetric and asymmetric stretching vibration of the *gem*-dicarbonyl $[Rh^+(CO)_2]$ complex on isolated Rh^+ sites (20, 21). In several studies, where interaction of rhodium catalysts with NO–CO mixtures was investigated, bands in the region of 2090 cm^{-1} have been attributed to the asymmetric ν(CO) vibration of a Rh(CO)(NO) species (6, 10, 22). However, the absence of

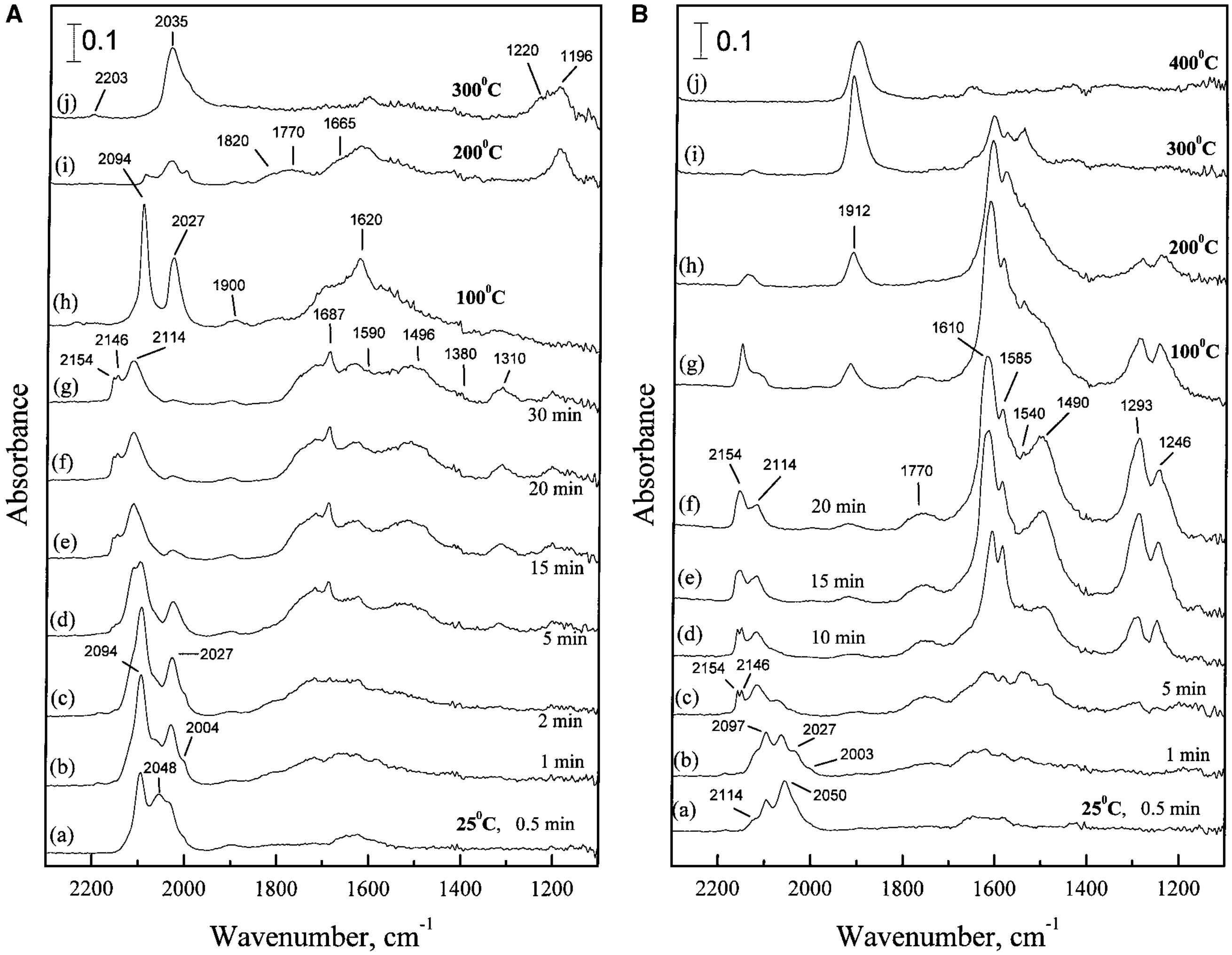


FIG. 2. (A) FTIR spectra recorded following interaction of 0.25% NO–0.5% CO (in Ar) with reduced Rh/TiO_2 at room temperature (a–g), and subsequent stepwise heating to 100, 200, and 300°C in the presence of the reaction mixture (h–j). (B) FTIR spectra recorded following interaction of 0.25% NO–0.5% CO–1% O_2 (in Ar) with reduced Rh/TiO_2 at room temperature (a–f) and subsequent stepwise heating to 100, 200, 300, and 400°C in the presence of the reaction mixture (g–j).

an accompanying absorption band in the 1730–1750 cm^{-1} region, in all experiments presented here, excludes the existence of this "fraternal" species under the experimental conditions employed.

Increasing the time of exposure to 1 and 2 min results in a progressive decrease of the intensity of the 2048 cm^{-1} band and in a parallel increase of the intensities of the bands at 2094 and 2027 cm^{-1} (Fig. 2A, b–c). Prolonged exposure (15–30 min) to the NO–CO mixture leads to a significant suppression of the intensity of the bands mentioned above and to the development of new ones located at 2154, 2146, and 2114 cm^{-1} (Fig. 2A, d–g). The bands at 2146 and 2114 cm^{-1} appear in the spectral region where carbonyl species linearly bonded on oxidized rhodium sites are expected to adsorb (20, 21), and have been also observed in previous studies following CO adsorption on the present catalyst (23, 24). In agreement with the results of these studies and the work of Rice *et al.* (21), the bands observed at ca. 2146 and 2114 cm^{-1} are attributed to Rh^{3+}–CO and Rh^{2+}–CO species, respectively. As will be discussed below, the band at 2154 cm^{-1} may be assigned to Rh–CN.

Increasing the reaction temperature to 100°C (Fig. 2A, h) results in the disappearance of the bands above 2100 cm^{-1} and development of the *gem*-dicarbonyl bands at 2094 and 2027 cm^{-1}, which now dominate the spectrum. A further increase of temperature to 200 and 300°C leads to a decrease and disappearance, respectively, of the 2094/2027 cm^{-1} bands and to progressive growth of the Rh^0–CO band, which now appears at 2035 cm^{-1}. The latter band is coverage dependent, due to bipolar coupling of adsorbed CO molecules and, depending on the experimental conditions, it appears in the region of 2030–2050 cm^{-1} in the spectra of the present study.

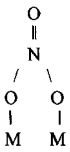
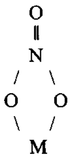
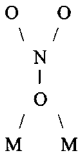
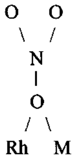
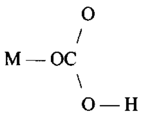
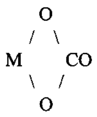
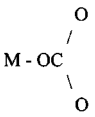
Apart from the carbonyl bands discussed above, several more bands appear in the spectra following exposure of the catalyst to the NO–CO mixture at RT. The bands appearing in the region of ca. 1950–1650 cm^{-1} are generally attributable to NO species adsorbed on Rh, while the broad features located below 1650 cm^{-1} are due to nitrogen- and carbon-containing species associated with the support (Table 1). As will be discussed below, the weak band located at 2203 cm^{-1}, which is observed only at 300°C (Fig. 2A, j), is attributed to isocyanate adsorbed on Rh. The weak band at ca. 1900 cm^{-1}, which is present in the spectra obtained at RT and 100°C (Fig. 2A, a–h), is attributed to Rh–NO^+ (4–19). However, part of this band could be due to bridge-bonded CO on reduced Rh sites [$(Rh^0)_2CO$], which is expected to absorb at ca. 1885 cm^{-1} (20, 21). The 1900 cm^{-1} band disappears upon the sample being heated above 200°C. Three more bands due to adsorbed nitrogen oxide species can be distinguished, located at ca. 1820, 1770, and 1665 cm^{-1}. These bands, which are best observed at 200°C (Fig. 2A, i), are attributed to Rh–NO and Rh–NO^-(high) and Rh–NO^-(low) species, respectively [(18, 19) and references therein]. Concerning the spectral features below 1700 cm^{-1}, one can distinguish bands at ca. 1687, 1590, 1380, and 1310 cm^{-1} as well as bands at ca. 1620 and 1435 cm^{-1} due to carbonate and bicarbonate species, respectively (Fig. 2A, Table 1). Assignment of these bands is based on the work of Rethwisch and Dumesic (25), who studied by IR spectroscopy the CO/CO_2 adsorptive properties of a series of oxides, including TiO_2. It should be noted that the appearance of many overlapping bands in the 1700–1100 cm^{-1} region makes unequivocal assignment of these spectral features difficult. All these bands decrease in intensity with increasing temperature and disappear at 300°C. A new band appears at 1196 cm^{-1} upon heating at 200°C and a high-temperature shoulder at 1220 cm^{-1} becomes distinguishable at 300°C (Fig. 2A, i–j). The origin of these bands will be discussed below.

The corresponding spectra obtained in the presence of O_2 in the feed are presented in Fig. 2B. Interaction of the reduced catalyst with the NO–CO–O_2 mixture at RT leads to the development of carbonyl bands at ca. 2050 (Rh^0–CO) and 2094/2027 [$Rh(CO)_2$] cm^{-1}, which progressively disappear with time on stream, giving rise to bands at 2146 (Rh^{3+}–CO), 2114 (Rh^{2+}–CO), and 2154 cm^{-1} (Fig. 2B, a–f). The last band, which appears together with the one attributed to Rh^{2+}–CO, was also observed during the TPSR experiments in the absence of O_2 (Fig. 2A) and occurs in the frequency region where adsorbed cyanide species are expected to appear. Srinivas *et al.* (14) observed analogous bands at ca. 2120 and 2160 cm^{-1} following interaction of NO–CO with Rh/SiO_2 at 100°C and attributed them to Rh^{2+}–CO and Rh–CN, respectively. Solymosi *et al.* (7) also observed a band at 2145 cm^{-1} following exposure of Rh/Al_2O_3 to NO–CO at room temperature, which was attributed to adsorbed cyanide ion. Kaspar *et al.* (11) also attributed a band observed at 2045 cm^{-1} in the presence of flowing NO/CO mixture at 200°C to a Rh–CN species. Similarly, Dictor (8) attributed a band located at 2150–2130 cm^{-1} to adsorbed cyanide produced by removal of an O atom from adsorbed isocyanate. The band observed in the present study at 2154 cm^{-1} is more pronounced and stable when oxygen is added in the feed (compare spectra of Fig. 2A with those of Fig. 2B). Since cyanide species are expected to be more stable under oxidizing than under reducing conditions, and in agreement with the literature results discussed above, the 2154 cm^{-1} band is tentatively assigned to Rh–CN.

Bands due to nitrosyl species, located at ca. 1912 and ca. 1770 cm^{-1}, also develop with time on stream (Fig. 2B, a–f). However, the spectra are now dominated by very intense bands due to species associated with the support, located at 1610, 1585, 1540, 1490, 1293, and 1246 cm^{-1}, which continuously increase in intensity and reach a plateau after 20 min on stream (Fig. 2B, a–f). All of these spectral features were observed in a previous study (19), where the

TABLE 1

Assignment of FTIR Bands Observed Following Interaction of NO, CO, O_2, and Their Mixtures with 0.5% Rh/TiO_2

Adsorbed species	Frequency (cm^{-1})	Description	Ref.
Rh–NO^+	1895–1912	Positively charged	4–19 and references therein
Rh–NO	1820	Neutral	
Rh–NO^-(low)	1665	Negatively charged	
Rh–NO^-(high)	1770	Negatively charged	
$Rh(NO)_2$	1830 (ν_{sym}) 1728 (ν_{asym})	*gem*-Dinitrosyl	
Rh^0–CO	2030–2050	Linear CO	20–24
Rh^+–CO	2075		
Rh^{2+}–CO	2114		
Rh^{3+}–CO	2140–2146		
$(Rh^0)_2CO$	1885	Bridge-bonded CO	
$(Rh^+)_2CO$	1995		
$(Rh^{2+})_2CO$	2004		
$Rh^+(CO)_2$	2094 (ν_{sym}) 2027 (ν_{asym})	*gem*-Dicarbonyl	
Rh–NCO	2203 (ν_{sym}) 1477 (ν_{asym})	Isocyanate	26
Rh–CN	~2154 (broad)	Cyanide	7, 8, 11, 14
–NO_2^+	2120–2145	Nitronium (NO_2^+)	27
	1610 1246	Nitrate species associated with the support	19 and references therein
	1585 1293		
	1540 1290		
	1490		
	1620 1435	Bicarbonate	25
 or 	1687 1590 1380 1310	Carbonate	
TiO_{2-x}	1220 1196	Reduced TiO_2 species	28

interaction of NO with Rh/TiO_2 and $Rh/TiO_2(W^{6+})$ catalysts was investigated, and were attributed to four differently coordinated $NO_{3(a)}$ species associated with the support (Table 1). Comparison of Figs. 2A and 2B indicates that formation of these species is strongly favored by the presence of oxygen in the feed.

The stepwise increase of reaction temperature to 400°C affects differently the different adsorbed species (Fig. 2B, g–j). The bands at 2154, 2146, and 2114 cm^{-1} continuously decrease in intensity and disappear at temperatures higher than 300°C. This is also the case for the bands below 1650 cm^{-1}, which progressively decrease in intensity with increasing temperature before disappearing at 400°C. The nitrosyl band at ca. 1770 cm^{-1} is present at 100°C but disappears at higher temperatures. However, the band at ca. 1912 cm^{-1}, attributed to $Rh–NO^+$, increases with increasing temperature up to 300°C. A further increase of temperature to 400°C causes a small decrease in the band's intensity. It is observed that, at temperatures above 200°C, the surface is covered by positively charged NO species when oxygen is added to the feed. In the absence of oxygen, the surface is covered by CO molecules on reduced Rh sites (Fig. 2A). The bands at 1220 and 1196 cm^{-1} observed in the absence of O_2 in the feed are not observed in the spectra of Fig. 2B.

3.3. *Interaction of CO–NO and NO–CO–O_2 Mixtures with Reduced Rh/TiO_2 at 250°C*

A series of FTIR and transient MS experiments was conducted at 250°C in order to examine the formation, relative population, thermal stability, and reactivity of adsorbed species. The temperature of 250°C was chosen because, at this temperature, both reduction products are formed (N_2 and N_2O), as observed in Fig. 1. Furthermore, preliminary experiments showed that at higher reaction temperatures the population of the adsorbed species is reduced, resulting in a significant decrease of the corresponding IR band intensities, thus making observations more difficult.

The IR spectra obtained following exposure of the reduced Rh/TiO_2 catalyst to the 0.5% CO–0.25% NO/Ar mixture are shown in Fig. 3A. It is observed that immediately after exposure to the reaction mixture, a strong band at 1912 cm^{-1} appears in the spectrum, accompanied by bands at 1616, 1540, and 1435 cm^{-1} (Fig. 3A, a). The 1912 cm^{-1} band, attributed to $Rh–NO^+$, progressively decreases in intensity and disappears after 5–8 min on stream (Fig. 3A, a–d). It is only then that bands at 2203, 2075, 2037 2004(sh), and 1995 cm^{-1} appear in the spectrum and gradually develop with time on stream (Fig. 3A, d–m). Development of these bands is accompanied by the appearance and growth of three more bands located at 1477, 1220, and 1196 cm^{-1}. It is interesting to notice that the feature located at 2203 cm^{-1} was only weakly observed in the TPSR experiments of Fig. 2A.

The band at ca. 2075 cm^{-1} appears in the frequency region where CO species linearly bonded with oxidized rhodium sites absorb, and may be attributed to $Rh^+–CO$ (20, 21). The bands located at 2004 and 1995 cm^{-1} are positioned between the bands of the linear- (2030–2050 cm^{-1}) and bridge-bonded (1885 cm^{-1}) CO adsorbed on Rh^0 sites. Rice *et al.* (21) postulated that bands in this vicinity should arise from bridged-type species adsorbed on oxidized rhodium sites. Following this postulation, and in agreement with work conducted in this (23) and other laboratories (24) using the present catalyst, the 2004 and 1995 cm^{-1} bands are assigned to $(Rh^{2+})_2CO$ and $(Rh^+)_2CO$ species, respectively.

The IR feature at 2203 cm^{-1} is too intense to be attributed to CO adsorbed on oxidized Rh sites. It is generally agreed that IR bands in this region are due to isocyanate species adsorbed on rhodium, since all transition metal isocyanate complexes exhibit bands between 2230 and 2170 cm^{-1}, due to symmetric stretching of the –NCO group ((26) and references therein). Isocyanate species attached to the support generally appear at higher frequencies, in the region of 2300–2265 cm^{-1}. In the FTIR experiments of the present study, development/disappearance of the 2203 cm^{-1} band is always accompanied by a similar behavior of a smaller band located at ca. 1477 cm^{-1}, which should correspond to the asymmetric vibration of the –NCO group (26). Therefore, the bands at 2203 and 1477 cm^{-1} are attributed to the asymmetric and symmetric stretching vibrations, respectively, of Rh–NCO.

The stability of the surface species formed upon interaction of the catalyst with the NO–CO mixture at 250°C has been investigated by monitoring the alteration of IR band intensities, under Ar flow, with time on stream. Results are shown in Fig. 3B, a–j. It is observed that switching from CO–NO to Ar flow at 250°C leads to a progressive decrease of the intensity of the Rh–NCO band at 2203 cm^{-1}, which disappears after ca. 10 min on stream (Fig. 3B, b–e). In contrast, the bands in the region of 2100–1990 cm^{-1}, attributed to carbonyls adsorbed on Rh, increase in intensity, probably at the expense of the 2203 cm^{-1} band, implying a possible interconversion of the corresponding species. The band at 1665 cm^{-1}, attributed to $Rh–NO^-$(low), disappears immediately upon the flow being switched to Ar, while the bands located below 1650 cm^{-1} are very stable and cannot be completely removed by isothermal treatment in Ar flow for 20 min (Fig. 3B, b–g). The corresponding species can be removed from the surface only after the sample is heated in Ar flow at temperatures above 400°C, except from those responsible for the absorption features at 1220/1196 cm^{-1} (Fig. 3B, h–j).

The interaction of the reduced Rh/TiO_2 catalyst with a 0.5% CO–0.25% NO (in He) mixture at 250°C was also examined with the transient MS technique, in order to investigate the transient gas-phase behavior of reactants and products. As observed in Fig. 3C, immediately after the

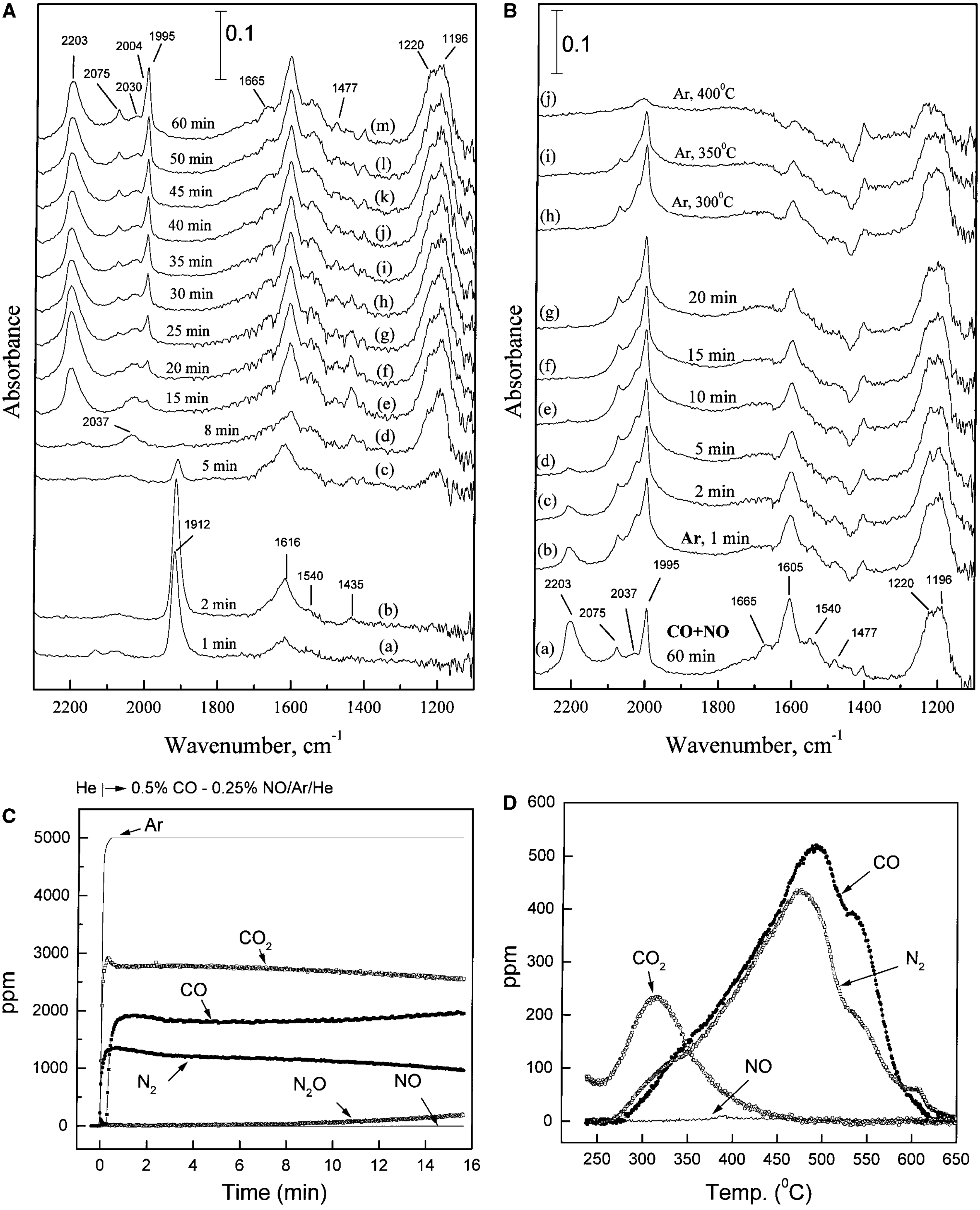


FIG. 3. FTIR spectra obtained as a function of time on stream following (A) interaction of the reduced catalyst with 0.25% NO–0.5% CO (in Ar) at 250°C for 60 min, and (B) subsequent thermal treatment under Ar flow. (C) Transient MS responses of reactants and products obtained after the switch He → 0.25% NO–0.5% CO (in He) at 250°C, followed by purging with He for 5 min and (D) subsequent TPD of adsorbed species.

He → NO/CO switch, only CO_2 and N_2 are obtained at the exit of the reactor, while CO appears after ca. 20 s on stream. The responses of CO, CO_2, and N_2 do not change significantly during the next few minutes. However, after about 10 min on stream, N_2O formation is observed which slowly increases with time of exposure. When this happens, the yields of CO_2 and N_2 progressively decrease with time on stream, while that of CO increases (Fig. 3C). Comparison with the corresponding FTIR spectra of Fig. 3A shows that formation of nitrous oxide in the gas phase coincides with the development of the bands due to isocyanate species and carbonyls on oxidized sites on the catalyst surface.

The TPD curves of the surface species accumulated on the catalyst under reaction conditions are presented in Fig. 3D. CO_2 desorbs between 200 and 450°C, exhibiting a single peak with its maximum located at 310°C. CO and N_2 start desorbing together at ca. 270°C and their TPD curves follow the same trend. The response of N_2 exhibits a maximum at ca. 470°C, while a low-temperature shoulder of the principal peak may also be distinguished at ca. 350°C. The response of CO reaches a maximum at 490°C and then drops, following the response of N_2. The amounts of desorbed species are given in Table 2.

Similar FTIR and transient MS experiments were also conducted with the presence of oxygen in the feed and the spectra obtained are presented in Fig. 4. It is apparent that the presence of oxygen drastically alters the spectra. Immediately after exposure of the reduced catalyst to NO–CO–O_2 mixture (Fig. 4A, a), several bands appear in the spectrum at 2140 and 2098 (CO on oxidized Rh sites), 1908 (Rh–NO^+), 1830, 1728, 1650, and 1614 cm^{-1}, the latter two attributed to carbonate species associated with the support. Bands at 1830 and 1728 cm^{-1} have been previously attributed to the symmetric and asymmetric vibrations, respectively, of a dinitrosyl complex (18). This assignment has been confirmed with the use of isotopic ^{15}NO–^{14}NO mixtures, and results will be presented separately. Prolonged exposure results in the appearance of additional bands at ca. 1540 and 1435 cm^{-1} (Fig. 4A, a–e), due to species associated with the support (Table 1). The band at 2140 cm^{-1} continuously increases in intensity with time on stream, while that at ca. 2098 cm^{-1} now appears as a shoulder of the 2140 cm^{-1} band. The bands at 1908, 1830, and 1728 cm^{-1} slightly decrease in intensity after more than 2 min on stream, when the bands at 1540 and 1435 cm^{-1} start to develop. These bands are thermally stable and do not decrease in intensity following isothermal treatment with Ar for 30 min, except the bands above 2100 cm^{-1} which immediately disappear from the spectrum following the switch to Ar flow (Fig. 4A, f–h).

TABLE 2

Amounts of Species Desorbed from 0.5% Rh/TiO_2 in the TPD Experiments

Pretreatment	Fig. no.	Amounts of species desorbed (μmol/g_{cat})				
		CO	CO_2	NO	N_2	N_2O
He → NO/CO	3D	44.6	12.7	0	36.8	0
He → NO/CO/O_2	4C	0	0.7	4.7	1.3	0
He → NO/CO → He → CO	5C	15.4	4.6	0	11.7	0
He → NO/CO → He → NO	6C	0	1.0	1.1	8.6	0
He → NO/CO → He → O_2	7C	0	0.8	0.6	4.3	0

The responses obtained after the switch He → NO–CO–O_2 are presented in Fig. 4B, which show immediate appearance of CO_2, NO, N_2, and negligible amounts of N_2O in the gas phase, reaching constant concentrations after a short period of time (Fig. 4B). In the subsequent TPD experiment, only NO is observed to desorb, giving two peaks at 320 and 370°C (Fig. 4C).

3.4. Reactivity of Surface Species Formed under NO–CO Reaction Conditions

The reactivity of the adsorbed species formed under CO–NO reaction conditions at 250°C was investigated by monitoring the change of the IR bands, obtained following treatment of the catalysts with NO/CO mixtures, upon switching to CO, NO, or O_2 flow.

Reactivity toward CO. The FTIR spectrum obtained following interaction of the Rh/TiO_2 catalyst with the CO–NO mixture at 250°C for 30 min is shown in Fig. 5A-a. This spectrum is similar to the corresponding one presented in Fig. 3B-a, obtained following the same treatment. Purging with Ar flow for 2 min and exposure of the catalyst surface to 0.5% CO/Ar flow results initially in the growth of the 2203 cm^{-1} band, which then decreases with time and disappears after 10 min on stream (Fig. 5A, b–f). The intensities of the carbonyl bands at 2100–1990 cm^{-1} do not significantly change with time on stream, except for the one at ca. 2040 cm^{-1}, attributed to Rh^0–CO, the relative intensity of which increases with time of exposure. This is more pronounced after 30 min under CO flow (Fig. 5A, g) and indicates the slow reduction of the catalyst surface with time on stream. Interestingly, the bands located at 1220/1196 cm^{-1} are not significantly influenced by interaction with CO.

Concerning the gas phase, introduction of 0.25% CO/He flow over the catalyst previously treated with the CO–NO mixture at 250°C, leads to the production of only small amounts of CO_2 and N_2 (Fig. 5B). The TPD spectra obtained following this treatment are shown in Fig. 5C, where the gas-phase concentrations of CO_2, CO, NO, and N_2 are plotted as a function of temperature. The amounts of the species desorbed are listed in Table 2. CO desorbs exhibiting two peaks located at ca. 350 and 480°C. Relatively small amounts of CO_2 are desorbed in the region of 250 to 450°C, while N_2 desorbs in a single, symmetric peak located at 450°C (Fig. 5C).

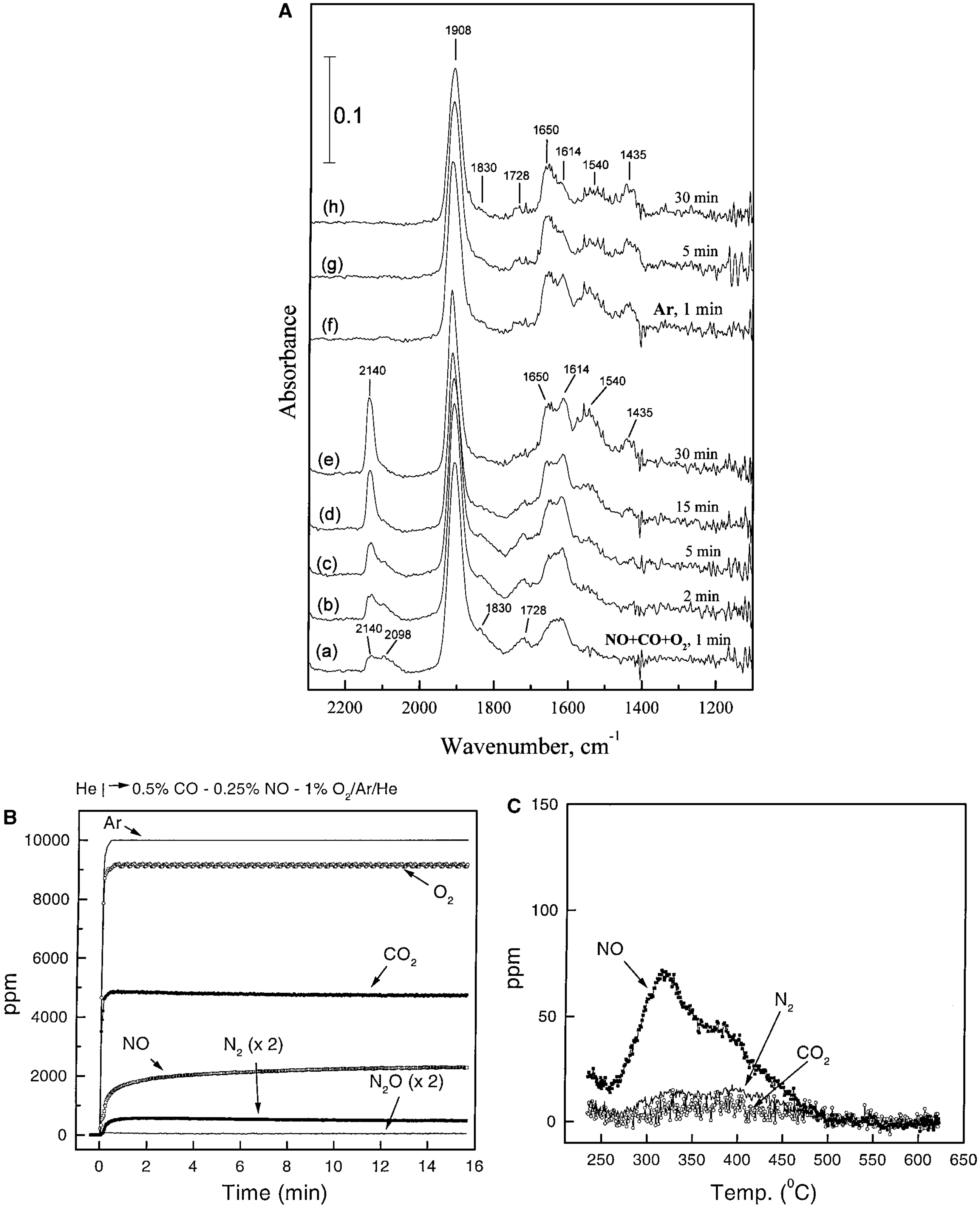


FIG. 4. (A) FTIR spectra obtained as a function of time on stream following interaction of the reduced catalyst with 0.25% NO–0.5% CO–1% O_2 (in Ar) at 250°C for 30 min (a–e), followed by isothermal treatment with Ar (f–h). (B) Transient MS responses of reactants and products obtained after the switch He → 0.25% NO–0.5% CO–1% O_2 (in He) at 250°C, followed by purging with He for 5 min and (C) subsequent TPD of adsorbed species.

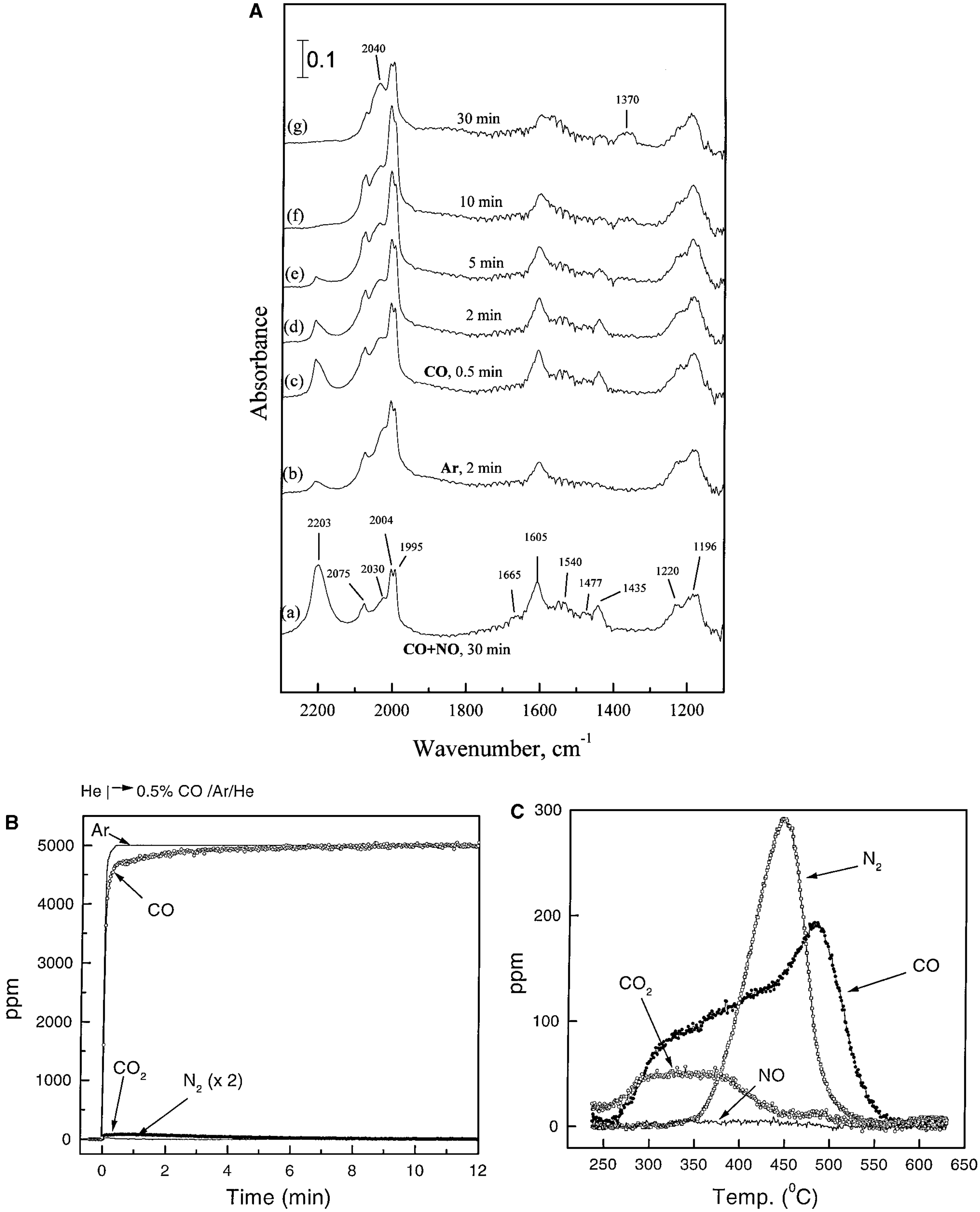


FIG. 5. (A) FTIR spectra obtained following interaction of the reduced catalyst with 0.25% NO–0.5% CO (in Ar) at 250°C for 30 min (a), followed by purging with Ar for 2 min (b) and switch to CO (0.5% in Ar) flow for 30 min (c–g). (B) Transient responses of reactants and products obtained after the switch He → 0.5% CO/He over catalysts previously treated with 0.25% NO–0.5% CO (in He) at 250°C, followed by (C) purging with He for 5 min and subsequent TPD of adsorbed species.

Reactivity toward NO. The FTIR spectra obtained following interaction of the surface species formed under CO–NO reaction conditions at 250°C with NO are presented in Fig. 6A. Switching from Ar flow to 0.25% NO/Ar leads to an immediate disappearance of the 2203 cm^{-1} band (Fig. 6A, c). After 1 min on stream, only small amounts of adsorbed carbonyls (2100–1995 cm^{-1}) are present on the surface, which completely disappear after 3 min on stream (Fig. 6A, d). On the other hand, new bands appear in the spectrum immediately after the switch to NO, which are located at 1895, 1770 (broad), and 1665 cm^{-1} (Fig. 6A, c). The intensity of the band at 1895 cm^{-1}, attributed to $Rh–NO^+$, gradually increases with time on stream and reaches a plateau after 10 min. Development of this band is accompanied by a progressive shift of its maximum from 1895 to 1912 cm^{-1} with increasing coverage (Fig. 6A, c–h). The week bands located at 1770 (broad) and 1665 cm^{-1}, attributed to $Rh–NO^-$(high) and $Rh–NO^-$(low), respectively, which appear immediately following introduction of NO, are present only during the first minutes of the transient and decrease with time on stream before disappearing after 5–10 min (Fig. 6A, c–f). It is only when these bands disappear from the spectrum that the 1830 and 1728 cm^{-1} bands, attributed to $Rh(NO)_2$, develop (Fig. 6A, f–h). The band at 1540 cm^{-1} also appears in the spectrum and develops only when the 1912 cm^{-1} band reaches its maximum intensity (Fig. 6A, f–h). The 1220/1196 cm^{-1} bands decrease in intensity with time on stream and disappear after less than 10 min (Fig. 6A, b–f). A broad band, located above 2100 cm^{-1}, becomes discernible when the carbonyl species are removed from the surface following interaction with NO and is initially located at ca. 2120 cm^{-1} (Fig. 6A, d). The intensity of this band does not significantly change with time on stream, but it gradually shifts to higher frequencies, up to 2145 cm^{-1} (Fig. 6A, c–h).

The transient responses of NO, N_2, N_2O, CO_2, and Ar obtained following the switch He → 0.25% NO/He over the Rh/TiO_2 catalyst previously exposed for 10 min to the CO–NO mixture at 250°C are shown in Fig. 6B. It is observed that NO appears at the exit of the reactor only after ca. 6.0 min on stream. Immediately after the switch, only CO_2 and N_2 appear in the gas phase and reach a plateau. The yield of CO_2 rapidly decreases after ca. 2.5 min on stream, while N_2 formation continues for about 6 min. When the yield of N_2 starts to decrease, N_2O formation initiates and peaks at ca. 6.2 min on stream. This happens when NO appears at the exit of the reactor.

The amounts of N_2, N_2O, and CO_2 formed during this experiment are shown in Table 3. For comparison, the amounts of products formed following interaction of NO with H_2-reduced and CO-precovered catalysts [Ref. (18)] are also shown. It is observed that the amount of N_2 formed following the switch to NO strongly depends on the pretreatment and is maximized for the CO–NO-pretreated sample. In contrast, the amount of N_2O formed in the same experiments is more or less constant, and does not depend on pretreatment (Table 3). In the subsequent TPD experiment (Fig. 6C), only small amounts of NO and CO_2 desorb with maxima at ca. 300 and 360°C, respectively. The dominant TPD peak is due to N_2, which exhibits a relatively intense peak at ca. 340°C and a smaller one at ca. 420°C. The amounts of desorbed species are shown in Table 2.

TABLE 3

Amounts of N_2O, N_2, CO, and CO_2 Formed Following Interaction of NO with Differently Pretreated Rh/TiO_2 Catalysts at 250°C

Pretreatment	Ref.	Amounts of species formed ($\mu mol/g_{cat}$)			
		CO	CO_2	N_2	N_2O
H_2 reduction, 250°C, 1 h	(18)			11.1	5.1
H_2 reduction, 250°C, 1 h + CO adsorption, 250°C, 12 min	(18)	0	13.8	20.7	7.1
H_2 reduction, 250°C, 1 h + NO/CO reaction, 250°C, 15 min	This work	0	33.8	128.5	6.7

Reactivity toward O_2. The FTIR spectra obtained following interaction of 1% O_2 with a 0.5% Rh/TiO_2 catalyst previously treated with NO–CO for 30 min at 250°C are shown in Fig. 7A. Switching the flow to 1% O_2/Ar results in the disappearance of the bands at 2203 and 2100–1990 cm^{-1} in less than 1 min (Fig. 7A, c) and 2 min on stream (Fig. 7A, d), respectively. The only band due to adsorbed nitrosyl species which is observable under O_2 flow is a very weak one at ca. 1905 cm^{-1}, which remains on the surface even after 5 min on stream. The bands below 1650 cm^{-1}, although decreased in intensity, are not completely removed from the spectra after 10 min on stream (Fig. 7A, f).

The broad band, which was also observed in Fig. 6A, appears again immediately after the switch to O_2 at ca. 2120 cm^{-1}, and shifts to 2135 cm^{-1} with time on stream. This band is of uncertain origin. Hoost *et al.* (27) attributed a band located at 2133 cm^{-1} to a surface nitronium (NO_2^+) species. Based on these findings, and since the 2145–2120 cm^{-1} band is observed only following interaction of surface species with oxidants (Figs. 6A and 7A), it is tentatively assigned to $(NO_2^+)_a$ species, associated with the support.

The bands at 1220/1196 cm^{-1} decrease with time on stream and disappear after more than 10 min of exposure (Fig. 7A). These bands appear in several of the spectra presented here (Figs. 2A, 3A, 3B, 5A, 6A, 7A). Although bicarbonates bonded on TiO_2 may absorb at ca. 1220 cm^{-1}, development of the 1220/1196 cm^{-1} bands observed in the present study cannot be attributed to such a species since their appearance/disappearance is not accompanied by similar behavior of bands at ca. 1620 and 1435 cm^{-1}. Careful

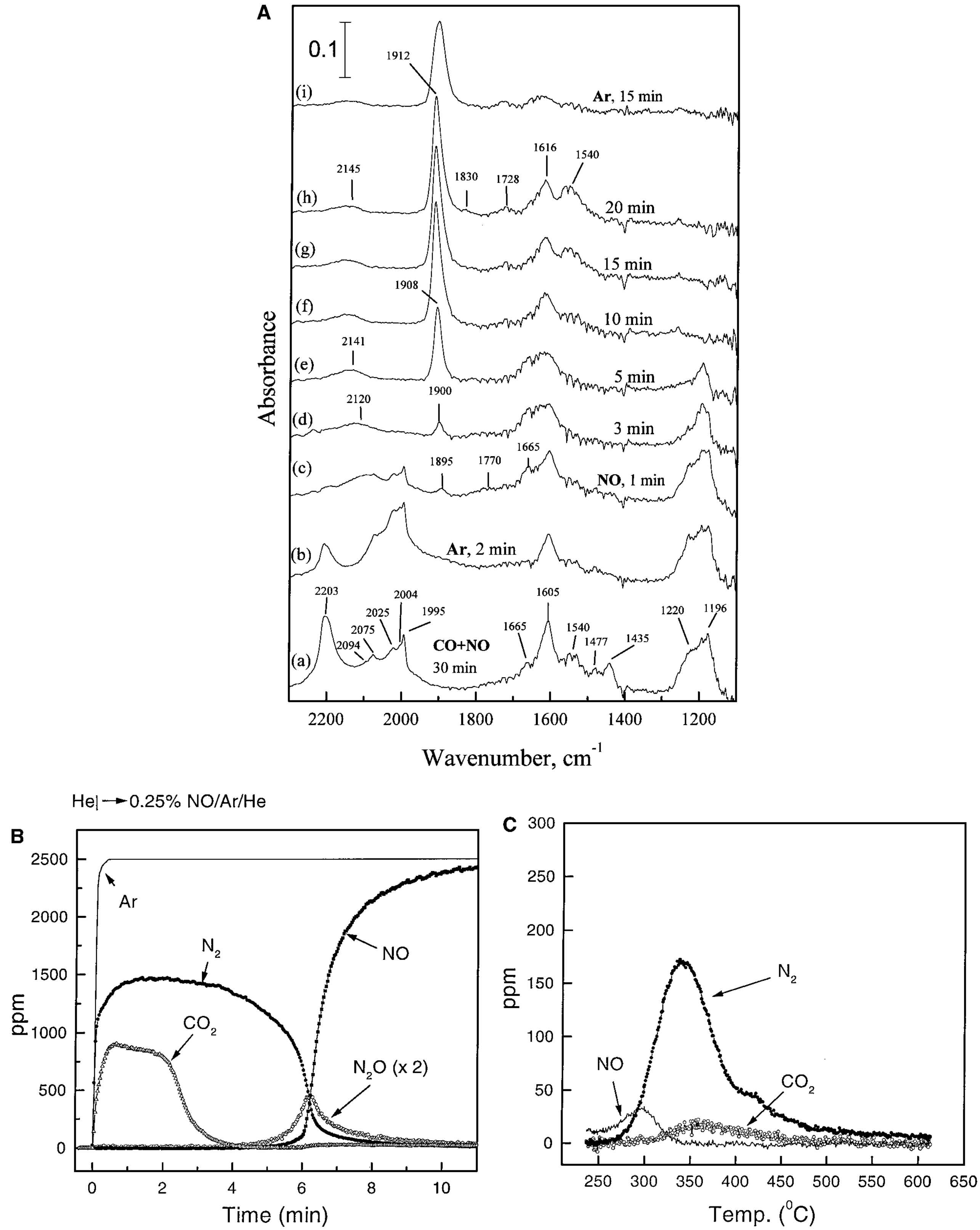


FIG. 6. (A) FTIR spectra obtained following interaction of the reduced catalyst with 0.25% NO–0.5% CO (in Ar) at 250°C for 30 min (a), followed by purging with Ar for 2 min (b), switch to NO (0.25% in Ar) flow for 20 min (c–h), and subsequent purging with Ar for 15 min (i). (B) Transient responses of reactants and products obtained after the switch He → 0.25% NO/He over catalysts previously treated with 0.25% NO–0.5% CO (in He) at 250°C, followed by (C) purging with He for 5 min and subsequent TPD of adsorbed species.

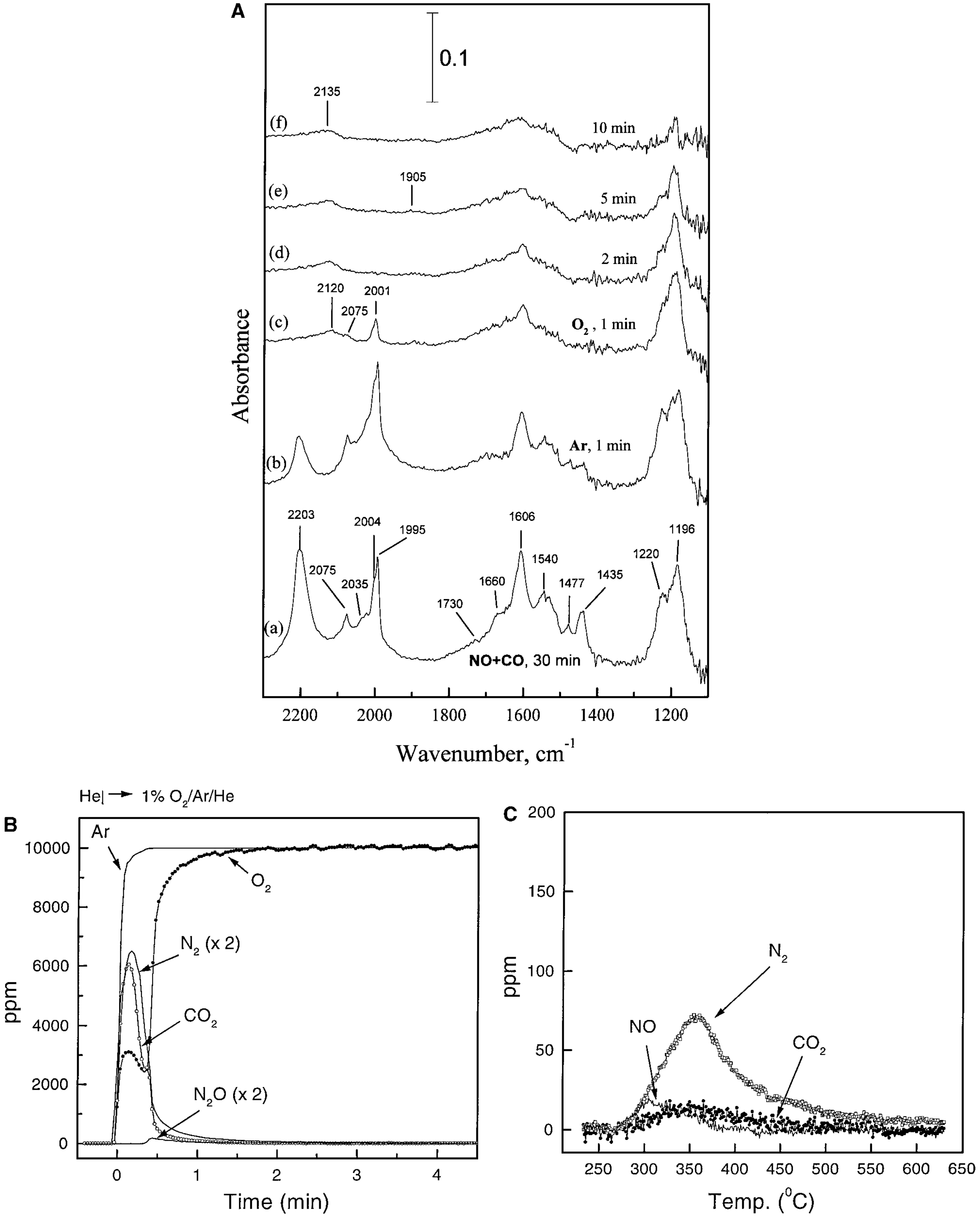


FIG. 7. FTIR spectra obtained following interaction of the reduced catalyst with 0.25% NO–0.5% CO (in Ar) at 250°C for 30 min (a), followed by purging with Ar for 1 min (b) and switch to O_2 (1.0% in Ar) flow for 10 min (c–f). (B) Transient responses of reactants and products obtained after the switch He → 1.0% O_2/He over catalysts previously treated with 0.25% NO–0.5% CO (in He) at 250°C, followed by (C) purging with He for 5 min and subsequent TPD of adsorbed species.

inspection of the spectra clearly shows that the bands at 1220/1196 cm^{-1} appear only under reducing conditions, i.e., under 0.25% NO–0.5% CO (Figs. 2A, 3A) flow and not under oxidizing conditions (Figs. 2B, 4A). These bands, once formed, are thermally very stable (Fig. 3B) and are not significantly influenced by subsequent treatment of the catalyst with CO at 250°C (Fig. 5A). In contrast, the bands progressively disappear from the spectra following treatment with NO (Fig. 6A) and O_2 (Fig. 7A) at the same temperature. Based on these results, the bands at 1220/1196 cm^{-1} may be correlated with phenomena associated with changes of the TiO_2 support. In their recent study on supported Pt catalysts, Bradford and Vannice (28) observed strong losses at 960/910 cm^{-1} in the DRIFT spectra obtained during H_2 reduction of Pt/TiO_2 at 500°C. These bands were attributed to Ti–O bond cleavage and TiO_x formation. Based on the above consideration, the 1220/1196 cm^{-1} bands observed in the present study to develop under reducing conditions could be attributed to rupture of Ti–O bonds and surface reduction of TiO_2. The shift of the vibrational frequencies from 960/910 to 1220/1196 cm^{-1} could be due to some kind of interaction of the support with rhodium in the vicinity of the metal crystallites.

The responses obtained following the switch He → 1% O_2 over a catalyst previously exposed to the CO–NO mixture for 10 min are shown in Fig. 7B. Immediately after the exposure, CO_2 is produced accompanied by evolution of N_2. After ca. 0.5 min a small amount of N_2O is formed. Then, no products can be detected, and O_2 concentration reaches that in the feed. In the subsequent TPD experiment, N_2 evolution is observed peaking at ca. 350°C, while only negligible amounts of NO and CO_2 are desorbed (Fig. 7C, Table 1).

4. DISCUSSION

4.1. *Reduction of NO by CO in the Presence and Absence of Oxygen*

Results presented in Fig. 2 show that the kind and relative population of surface species formed on the catalytic surface depend strongly on the reaction temperature and the presence of oxygen in the feed. This is also reflected in the catalytic activity and selectivity of Rh/TiO_2 for the reduction of NO by CO (Fig. 1). Interaction of NO–CO mixtures with the reduced 0.5% Rh/TiO_2 catalyst at RT initially results in the formation of *gem*-dicarbonyl and Rh^0–CO species, while weaker bands due to adsorbed NO species are also observed (Fig. 2A, a). Increasing time of exposure results in dissociation of adsorbed nitrogen oxide species and in the formation of adsorbed nitride and oxygen atoms. As has been discussed in our previous work (18), the latter species progressively oxidize the catalyst surface, which is evidenced by the progressive disappearance of Rh^0–CO and the further development of the $Rh(CO)_2$ bands. Prolonged exposure to the reaction mixture results in further oxidation of the surface and the dominance of carbonyls adsorbed on Rh^{2+} and Rh^{3+} sites. Oxidation of Rh takes place because atomic oxygen cannot be removed from the catalyst at RT by reaction with CO.

Heating to 100°C results in the reappearance of the *gem*-dicarbonyl species, which is the only carbonyl species observed (Fig. 2A, h). A further increase of the reaction temperature to 200°C leads to partial reduction of the surface, which is evidenced by the appearance of the Rh^0–CO band at 2035 cm^{-1} (Fig. 2A, i). The fact that the $Rh(CO)_2$ species is still present on the surface is in accordance with results of Solymosi *et al.* (7), who observed that in the presence of NO, reductive agglomeration of Rh^+ sites is greatly favored.

Bands due to Rh–NO, Rh–NO^-(high), and Rh–NO^-(low) become observable on the surface at 200°C (Fig. 2A, i). It is at this temperature that the catalyst becomes active toward NO reduction by CO. In our previous study, it was proposed that formation of dinitrogen in the gas phase occurs involving dissociation of negatively charged NO species through the following reactions:

$$Rh^0\text{–}NO^- + Rh^0 \rightarrow Rh\text{–}N + Rh\text{–}O \qquad [1]$$

$$Rh\text{–}N + Rh\text{–}N \rightarrow N_{2(g)} + 2Rh^0 \qquad [2]$$

$$Rh\text{–}NO^- + Rh\text{–}N \rightarrow N_{2(g)} + Rh\text{–}O + Rh^0. \qquad [3]$$

Formation of nitrous oxide has been found to occur involving the dinitrosyl complex, also requiring the presence of an adjacent reduced rhodium site:

$$Rh(NO)_2 + Rh^0 + NO \rightarrow Rh\text{–}NO^+ + Rh\text{–}O + N_2O_{(g)}. \qquad [4]$$

At RT, adsorbed atomic oxygen produced by Eqs. [1]–[4] cannot be removed from the surface, thus leading to the progressive oxidation of the surface, as clearly indicated by the development of several bands due to CO species adsorbed on oxidized Rh sites (Fig. 2A, a–g). However, at higher reaction temperatures, oxygen atoms are removed from the surface through reactions with CO or reduced titania species, and thus, the active Rh^0 sites are regenerated:

$$Rh\text{–}O + CO_{(g)} \rightarrow CO_{2(g)} + Rh^0 \qquad [5]$$

$$TiO_{2-x} + x Rh\text{–}O \rightarrow TiO_2 + x Rh^0. \qquad [6]$$

At temperatures above 300°C the catalyst surface is fully reduced by excess CO and the yield of N_2 reaches 100% (Fig. 1A).

The corresponding experiments, conducted in the presence of oxygen, show that interaction of the reaction mixture with the catalyst at RT leads to faster oxidation of rhodium, as evidenced by the formation of the carbonyls adsorbed on oxidized sites. In addition, development of large amounts of N-containing species on the support is also observed (Fig. 2B, a–f). Comparison of Figs. 2A and 2B shows that formation of carbon-containing species is favored under reducing conditions, while formation of N-containing species on the support is favored in the presence of oxygen. Increasing the temperature from 25 to 400°C results in a progressive decrease of the population of carbonyls, which disappear at temperatures above 200°C. This is due to reaction with oxygen, which starts above 100°C and reaches 100% conversion at 200–250°C (Fig. 1B). The presence of excess oxygen in the feed keeps most of the rhodium sites oxidized, as indicated by the absence of adsorbed species on Rh^0 sites.

Concerning adsorbed NO species, it is observed that only $Rh–NO^-$ and not $Rh–NO^+$ exists on the catalyst surface at RT, although part of the rhodium becomes oxidized with time on stream (Fig. 2B, a–f). This indicates that, under these conditions, NO is preferentially adsorbed on reduced sites, when available. Increasing the temperature results in a progressive increase of the population of $Rh–NO^+$ at the expense of the $Rh–NO^-$ species, which disappear above 100°C (Fig. 2B). As has been discussed in detail in the first paper of this series (18), the appearance of the $Rh–NO^+$ species takes place only when the population of $Rh–NO^-$ species starts to decrease, and it fully develops when the latter species disappears from the spectrum. Increasing the temperature to 400°C results in the disappearance of all bands, except for the one due to $Rh–NO^+$, which now dominates the spectrum (Fig. 2B, j). When this happens, dissociation of NO does not take place to a significant extent, resulting in the observed minimization of formation of reduction products (Fig. 1B).

4.2. *Transient Catalytic Behavior of Rh/TiO_2 at 250°C*

The transient FTIR spectra obtained following interaction of the NO–CO mixture with the reduced Rh/TiO_2 catalyst are initially dominated by the $Rh–NO^+$ band, which reaches its maximum intensity after ca. 2 min on stream and disappears after ca. 8 min (Fig. 3A). It is only then that bands due to Rh^0–CO and $Rh–NO^-$(low) appear in the spectrum, evidencing the presence of reduced rhodium sites. The intensities of these bands reach a maximum after ca. 15 min on stream and do not change further with time of exposure. The appearance of $Rh–NO^+$ during the first minutes of the transient indicates that dissociative adsorption of NO (Eq. [1]) and, concomitantly, partial oxidation of Rh readily take place at 250°C. This is confirmed by the formation of dinitrogen in the gas phase immediately after the switch to NO–CO mixture (Fig. 3C). The absence of adsorbed CO species during this period indicates that either (i) NO adsorption/decomposition is much faster than CO adsorption on reduced sites and/or (ii) that the population of Rh^0–CO is very small due to fast reaction with Rh–O produced by dissociation of NO. Although both explanations are possible, the latter is confirmed by the immediate appearance of CO_2 in the gas phase (Fig. 3C).

When Rh^0–CO (2037 cm^{-1}) appears on the surface, formation of Rh–NCO (2203 cm^{-1}) also occurs. This observation is in accordance with the results of Dictor (8), who found that, on oxidized catalysts, Rh is first reduced by CO, which is followed by the simultaneous appearance of the linear CO and isocyanate bands (8). The –NCO band at 2203 cm^{-1} increases in intensity during the first 20 min of exposure and then slightly decreases with time on stream, when carbonyls on oxidized Rh sites (2075, 1995 cm^{-1}) appear in the spectra (Fig. 3A, c–m). The formation of the Rh–NCO species has been proposed to occur by the reaction of either gaseous or adsorbed CO with adsorbed nitrogen atoms produced by dissociative chemisorption of NO (26). This statement is in agreement with the results of Fig. 3A, which shows immediate formation of $Rh–NO^+$ species indicating NO dissociation on the catalyst surface (i.e., formation of Rh–N and Rh–O), followed by the development of carbonyl and –NCO species.

In the corresponding transient MS experiments, N_2 is the only nitrogen-containing product which appears at the effluent of the reactor during the first minutes (Fig. 3C). N_2O appears only after more than 8 min on stream, i.e., when the catalyst surface becomes partially oxidized. The yield of N_2O increases with time on stream at the expense of N_2. This provides additional evidence that formation of dinitrogen is favored on reduced Rh surfaces (Eqs. [1]–[3]), while that of nitrous oxide is favored over partially oxidized surfaces (Eq. [4]).

The presence of oxygen in the feed results in rapid oxidation of the catalyst surface, which is covered by $Rh–NO^+$, $Rh(NO)_2$, and carbonyls on oxidized sites (Fig. 4A). In contrast to the results obtained in the absence of oxygen in the feed (Fig. 3C), steady-state conditions are reached rapidly in the gas phase and NO conversion does not exceed 20% (Fig. 4B).

4.3. *Thermal Stability and Reactivity of Surface Species Formed upon Reduction of NO by CO*

The IR spectra of Fig. 3B clearly show that Rh–NCO is the least thermally stable species formed following NO–CO reaction at 250°C. Its band at 2203 cm^{-1} disappears under isothermal Ar flow, but at the same time there is a rise of the band intensities in the ν(C–O) region. This indicates that there is an interconversion between the Rh–NCO and Rh^0–CO species. This is probably accompanied by the formation of nitride:

$$Rh–NCO \leftrightarrow Rh^0–CO + Rh–N. \qquad [7]$$

In the corresponding TPD-MS experiment, large amounts of CO_2, CO, and N_2 desorb from the surface (Fig. 3D, Table 2). The following arguments can be made concerning the origin of the large amounts of N_2 species which desorb: In the corresponding FTIR experiments no molecularly adsorbed NO is observed to survive on the catalyst surface following purging with Ar (Fig. 3B). Therefore, the HT peak of N_2 observed in the TPD spectra of Fig. 3D most probably originates from associative desorption of Rh–N species:

$$2\text{Rh–N} \rightarrow 2\text{Rh} + N_{2(g)}. \qquad [8]$$

Part of N_2 may also be produced by decomposition of N-containing species associated with the support.

The CO_2 peak at 310°C may be related with the Rh^0–CO species, since the corresponding band at 2030–2050 cm^{-1} is the first which disappears from the spectra:

$$\text{Rh}^0\text{–CO} + \text{Rh–O} \rightarrow 2\text{Rh}^0 + CO_{2(g)}. \qquad [9]$$

Part of Rh^0–CO may originate from decomposition of isocyanate (Eq. [7]). As observed in Fig. 3B, the most stable surface species are carbonyls adsorbed on oxidized Rh sites. These species can be removed from the surface only after heating above 400°C (Fig. 3B, j), producing CO in the gas phase (Fig. 3D).

The amounts of species desorbed from the catalyst surface which has been treated with NO–CO–O_2 mixtures are much smaller than those observed in the absence of oxygen in the feed (Table 2). This implies that the majority of surface sites are occupied by adsorbed oxygen. As observed in Fig. 4C, the main desorbing species is NO, originating from the Rh–NO^+ and $Rh(NO)_2$ species present on the catalyst surface under reaction conditions (Fig. 4A).

The surface species formed under NO–CO reaction conditions at 250°C are not significantly influenced by switching to CO flow (Fig. 5A), since carbonyls are already the dominant surface species. It is observed that immediately after the switch to CO, the intensity of the Rh–NCO band at 2203 cm^{-1} initially increases and then decreases with time on stream (Fig. 5A, c–g). The increase may be attributed to the existence of a high population of adjacent N atoms and vacant sites on the surface before the addition of CO. Initially, isocyanate species are formed through interaction of preadsorbed nitrogen atoms with incoming CO (Eq. [7]). However, prolonged exposure to CO probably leads to associative desorption of N atoms, to removal of an amount of this species from the surface, and concomitantly, to a shift of reaction [7] to the right. Reduction of Rh then gradually takes place, which can be followed by the relative increase of the 2040 cm^{-1} band with time on stream (Fig. 5A, g). Treatment with CO does not result in the complete removal of N-containing species from the surface. This is evidenced by the large amounts of N_2 that desorb from the surface in the subsequent TPD experiment (Fig. 5C). The symmetric shape and the position of this peak strongly indicate that it originates from associative desorption of nitrogen atoms still adsorbed on Rh.

When the Rh/TiO_2 catalyst previously treated with the CO–NO mixture for 30 min is exposed to NO, the isocyanate and carbonyl species disappear from the IR spectrum in less than 3 min (Fig. 6A, b–d), indicating their high reactivity toward NO. Disappearance of these bands is accompanied by the production of CO_2 in the gas phase, which stops when the carbonyl species are removed from the surface (Fig. 6B). Negatively charged Rh–NO^- species are immediately formed on the reduced surface, as indicated by the bands at 1770 and 1665 cm^{-1} (Fig. 6A, c), and their presence is accompanied by evolution of dinitrogen in the gas phase (Fig. 6B). The reason for the production of such large amounts of N_2 in this experiment, even when carbonyls are removed from the surface and CO_2 formation stops, may be related to the presence of the 1220 and 1196 cm^{-1} bands in the corresponding FTIR spectra (Fig. 6A), related to TiO_{2-x} formed during reaction of NO–CO over the catalyst. As discussed above, the reduced support may act as a scavenger of oxygen atoms formed by dissociation of NO (Eq. [6]). Oxygen atoms formed by dissociation of Rh–NO^- are readily consumed to oxidize TiO_{2-x} to TiO_2. This prevents oxidation of Rh sites, leaving room for further adsorption/dissociation of gaseous nitrogen oxide, which is evidenced by the presence of the 1170 and 1665 cm^{-1} bands (Fig. 6A, c–e) and the production of dinitrogen in the gas phase. In addition, comparison of Figs. 6A and 6B clearly shows that formation of N_2 in the gas phase takes place as long as the 1220/1196 cm^{-1} bands are present in the IR spectra, indicating the ability of the support to scavenge oxygen atoms. At the same time, the intensity of the Rh–NO^+ band at 1895–1912 cm^{-1} remains very small, indicating the relatively small concentration of oxidized Rh sites. When the 1220/1196 cm^{-1} bands disappear from the spectrum (Fig. 6A, f), oxygen atoms cannot be removed from the catalyst surface, adsorption and dissociation of $RhNO^-$ stops, and the $RhNO^+$ band fully develops. This signals the cease of dinitrogen production, as observed in Fig. 6B.

Another point of interest is related to the amounts of N_2 and N_2O produced following interaction of 0.5% NO/He with differently pretreated catalyst surfaces (Table 3). It is observed that the amount of N_2O formed over H_2-reduced, CO-precovered, and CO–NO-treated surfaces is practically constant, i.e., 5.1, 7.1, and 6.7 $\mu mol/g_{cat}$, respectively. In contrast, the corresponding amounts of N_2 produced are 11.1, 20.7, and 128.8 $\mu mol/g_{cat}$ (Table 3). In all cases, N_2O is not formed during the initial steps of the transient; only when the surface becomes partially oxidized do the dinitrosyl species appear on the surface (e.g., Fig. 6A) and NO starts evolving at the exit of the reactor (e.g., Fig. 6B). These results indicate that N_2 and N_2O are most probably produced via different routes. The large amounts of N_2 produced following interaction of NO with CO-precovered and, especially, CO–NO-treated samples are due to the presence of large quantities of oxygen atom scavengers on the Rh surface (adsorbed CO) and the support (TiO_{2-x}), which results in prolonged dissociative adsorption of NO and, therefore, increased N_2 formation (Eqs. [1]–[3]). On the other hand, the fact that the amounts of N_2O formed do not depend on the presence of reducible material on the catalyst surface provides additional evidence that production of N_2O does not require dissociative adsorption of NO and the presence of Rh–N species (Eq. [4]).

Finally, the surface species formed under NO–CO reaction conditions at 250°C are very reactive toward O_2. Exposure to O_2 results in an immediate disappearance of the isocyanate and carbonyl bands which disappear after ca. 1 min on stream (Fig. 7A, c), due to oxidation to CO_2 (Fig. 7B). N_2 also desorbs, implying rapid displacement of adsorbed Rh–N species by oxygen. However, small amounts of N-containing species remain on the surface after this treatment, as indicated by the desorption of both NO and N_2 in the subsequent TPD experiments (Fig. 7C). Addition of oxygen also results in the progressive decrease in the intensity of the 1220/1196 cm^{-1} bands. However, this process is slower than the corresponding process under a flow of NO (Fig. 6A), indicating the higher oxidation activity of the latter species under the present experimental conditions.

4.4. *Mechanistic Implications*

Comparison of the catalytic performance of Rh/TiO_2 for NO reduction by CO in the presence and absence of oxygen in the feed clearly shows the dramatic loss of activity in the presence of oxygen. Similar is the effect of accumulation of atomic oxygen, produced by dissociative adsorption of NO, which has been examined in detail at 250°C (Figs. 3–7). It turns out that the poisoning effect of atomic oxygen is the same and is not affected by the nature of the oxidant (NO or O_2).

Concerning adsorbed isocyanate species, the results of the present study do not provide straightforward evidence of their exact role. The reason is the low thermal stability of this species: Rh–NCO is transformed to carbonyl and nitride during purging with Ar (Eq. [7]), making it difficult to study the products formed following interaction of this species with NO, CO, and O_2. On the other hand, Rh–NCO is present on the catalytic surface under all steady-state (Fig. 2A, j) and transient experiments (Figs. 3A, 5A, and 6A) where reduction products are formed in the gas phase, while it is not observable in the experiments obtained under lean conditions, where reduction of NO is minimized. Obviously, the presence of isocyanate is related with the existence of carbonyls adsorbed on reduced rhodium sites and the presence of vacant sites, both of which are needed for reduction of NO by CO: vacant sites are needed for the dissociative adsorption of NO and adsorbed CO for scavenging oxygen atoms from the catalyst surface. However, this behavior does not provide evidence on whether Rh–NCO is an active species or a spectator species. To further examine this issue, additional experiments have been conducted employing Rh catalysts supported on W^{6+}-doped TiO_2, since the latter catalyst has been found to stabilize adsorbed isocyanate species. Results will be presented in the third paper of this series.

Concerning the role of the various nitrosyl species adsorbed on Rh under reaction conditions, the results of this and a previous study (18) show that the presence of oxygen on the surface results in a decreased population of $Rh–NO^-$ and an increased population of $Rh(NO)_2$ and $Rh–NO^+$. $Rh–NO^+$ is inactive for the reduction of NO by CO. It is favored by the presence of oxygen in the feed and fully develops over oxidized surfaces where reduction of NO does not take place.

In all steady-state and transient experiments presented here, production of dinitrogen in the gas phase takes place only under conditions in which reduced Rh sites are available on the catalytic surface. It may be safely argued that formation of N_2 is associated with the presence of $Rh–NO^-$ species on the surface, which is the catalytically active species. Production of nitrous oxide is related with the development of the $Rh(NO)_2$ species and starts when the population of $Rh–NO^-$ decreases. Formation of N_2O also requires the presence of adjacent reduced Rh sites. When this is not the case, production of N_2O does not take place, even when dinitrosyl species are present on the surface.

Summarizing, the activity of Rh for the selective catalytic reduction of NO by CO is related to the presence of vacant reduced sites which enable dissociation of NO with intermediate formation of $Rh–NO^-$. Under fuel-rich conditions, this requirement is fulfilled, since CO reacts with adsorbed atomic oxygen and restores the active sites. Addition of excess oxygen in the feed leads to partial oxidation of rhodium, which hinders NO dissociation.

SUMMARY AND CONCLUSIONS

The results of the present study can be summarized as follows:

1. The activity of Rh/TiO_2 catalysts is hindered by accumulation of surface oxygen, originating from NO decomposition and/or gas-phase oxygen in the feed.
2. An oxygen atom scavenger is necessary under steady-state conditions to remove atomic oxygen from the surface and restore the catalytic properties. In the present experiments, this was achieved by adsorbed CO species. Under certain conditions, reduced TiO_{2-x} may also act as an oxygen atom scavenger. Reducibility of titania may be important in applications where the feed changes from lean to rich.
3. In the absence of oxygen in the feed, the catalyst surface is covered by carbonyls and surface carbonate species. Under lean burn conditions, nitrosyl species on Rh and nitrates on the support dominate.
4. Formation of isocyanate requires the presence of adjacent $Rh^0–CO$ and reduced Rh sites and there is an interconversion between Rh–NCO and $Rh^0–CO$ species. Although

no evidence was drawn that isocyanate is a catalytically active species, its formation is favored under conditions in which NO conversion to reduction products is observed.

5. Results of the present study provide additional evidence that N_2 formation is related to dissociative adsorption of Rh–NO^- and N_2O formation to the presence of $Rh(NO)_2$. In both cases, the presence of reduced Rh^0 sites is necessary.

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REFERENCES

1. Parvulescu, V. I., Grange, P., and Delmon, B., *Catal. Today* **46**, 233 (1998).
2. Shelef, M., and Graham, G. W., *Catal. Rev.-Sci. Eng.* **36**, 433 (1994).
3. Taylor, K. C., *Catal. Rev.-Sci. Eng.* **35**, 457 (1993).
4. Peden, C. H. F., Belton, D. N., and Schmieg, S. J., *J. Catal.* **155**, 204 (1995).
5. Permana, H., Ng, K. Y. S., Peden, C. H. F., Schmieg, S. J., Lambert, D. K., and Belton, D. N., *J. Catal.* **164**, 194 (1996).
6. Arai, H., and Tominaga, H., *J. Catal.* **43**, 131 (1976).
7. Solymosi, F., Bansagi, T., and Novak, E., *J. Catal.* **112**, 183 (1988).
8. Dictor, R., *J. Catal.* **109**, 89 (1988).
9. Hyde, E. A., and Rudham, R., *J. Chem. Soc., Faraday Trans.* **80**, 532 (1984).
10. Anderson, J. A., Millar, G. J., and Rochester, C. H., *J. Chem. Soc., Faraday Trans.* **86**, 571 (1990).
11. Kaspar, J., de Leitenburg, C., Fornasiero, P., Trovarelli, A., and Graziani, M., *J. Catal.* **146**, 136 (1994).
12. Chuang, S. S. C., and Tan, C.-D., *J. Catal.* **173**, 95 (1988).
13. Hecker, W. C., and Bell, A. T., *J. Catal.* **84**, 200 (1983).
14. Srinivas, G., Chuang, S. S. C., and Debnath, S., *J. Catal.* **148**, 748 (1994).
15. Krishnamurthy, R., and Chuang, S. S. C., *J. Phys. Chem.* **99**, 16727 (1995).
16. Krishnamurthy, R., Chuang, S. S. C., and Balakos, W. W., *J. Catal.* **157**, 512 (1995).
17. Chuang, S. S. C., and Tan, C.-D., *Catal. Today* **35**, 369 (1997).
18. Chafik, T., Kondarides, D. I., and Verykios, X. E., *J. Catal.* **190**, 446 (2000).
19. Chafik, T., Efstathiou, A. M., and Verykios, X. E., *J. Phys. Chem. B* **101**, 7968 (1997).
20. Yang, A. C., and Garland, C. W., *J. Phys. Chem.* **61**, 1504 (1957).
21. Rice, C. A., Worley, S. D., Curtis, C. W., Guin, J. A., and Tarrer, A. R., *J. Chem. Phys.* **74**, 6487 (1981).
22. Solymosi, F., and Sarkany, J., *Appl. Surf. Sci.* **3**, 68 (1979).
23. Zhang, Z. L., Kladi, A., and Verykios, X. E., *J. Mol. Catal.* **89**, 229 (1994).
24. Trautmann, S., and Baerns, M., *J. Catal.* **150**, 335 (1994).
25. Rethwisch, D. G., and Dumesic, J. A., *Langmuir* **2**, 73 (1986).
26. Hecker, W. C., and Bell, A. T., *J. Catal.* **85**, 389 (1984).
27. Hoost, T. E., Laframboise, K. A., and Otto, K., *Appl. Catal. B* **7**, 79 (1995).
28. Bradford, M. C. J., and Vannice, M. A., *J. Catal.* **173**, 157 (1998).