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Mechanistic study of the reduction of NO by C_3H_6 in the presence of oxygen over Rh/TiO_2 catalysts

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Abstract

The mechanism of selective reduction of NO by propylene has been examined over Rh/TiO_2 catalysts, in the absence and presence of oxygen in the feed, employing FT-IR and transient-MS techniques. It has been found that no direct interaction between NO and propylene is required for the reaction to proceed. Reduction of NO requires the presence of reduced rhodium sites and the role of the hydrocarbon is to remove adsorbed oxygen and restore the catalytically active sites. Oxidation of propylene and removal of atomic oxygen occurs via intermediate formation of acrolein and acrylate species, which eventually decompose to yield CO and carboxylates on the catalyst surface. The mechanism of activation of propylene does not depend on the nature of the oxidant (NO or O_2) and is the same in the absence and presence of oxygen in the feed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nitrogen monoxide; Propylene; Selective reduction; Rhodium; Titanium oxide; Acrolein; Reaction mechanism; Fourier transform infrared; Transient reactivity

1. Introduction

Selective catalytic reduction of NO by hydrocarbons (HC-SCR) has received considerable attention due to its potential use in lean-burn and diesel-fueled vehicles. The reaction has been examined over a large number of catalysts, mainly metal ion-exchanged zeolites, base metal oxides and supported metals, and results have been reviewed recently [1–3]. Supported noble metal catalysts are promising due to their high activity at low temperatures and their good sulfur resistance and tolerance toward steam, but are characterized by narrow temperature window of operation. Among these catalysts, platinum is very active at low temperatures and, therefore, widely studied. However, platinum catalysts are characterized by low selectivity towards the formation of N_2 versus N_2O. In contrast, Rh-containing catalysts require higher operating temperatures, compared to Pt, but exhibit superior performance as far as selectivity towards N_2 is concerned [1–3].

The mechanism of the SCR of NO by propylene over noble metal catalysts has been investigated by several authors, mainly over Pt catalysts [1–11]. Results are controversial and the proposed mechanisms suggest that the key step for the formation of reduction products is either: (a) dissociative adsorption of NO on reduced Pt sites [4,5], or (b) intermediate formation of complexes such as $C_tH_xO_yN_z$, $C_xH_yO_z$, –NCO and –CN [7–9], or (c) oxidation of NO to NO_2 [10–13]. Mechanistic studies of SCR of NO by propylene over Rh are relatively few and are restricted to Al_2O_3-supported catalysts [7,14,15].

In our recent work [16–19], a detailed investigation of the NO + CO reaction has been carried out over Rh catalysts supported on TiO_2 and $TiO_2(W^{6+})$ carriers, employing transient-MS and FT-IR techniques.

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The SCR of NO by propylene was also investigated over the same materials [20]. The reaction mechanism over Rh/TiO_2 catalyst is investigated in the present study employing transient FT-IR spectroscopy and mass spectrometry (MS).

2. Experimental

The Rh/TiO_2 catalyst, with a metal loading of 1 wt.%, was prepared following the wet impregnation method using TiO_2 (Degussa P-25) and rhodium nitrate (Alfa Products) as starting materials, following a procedure that has been described earlier [16]. Prior to impregnation, the carrier was calcined at 700 °C for 5 h, which resulted in complete transformation of TiO_2 to its rutile form. The specific surface area of the catalyst was $13\,m^2/g$ and the metal dispersion, determined by H_2-chemisorption at room temperature, was found to be 30%.

The apparatus and procedures employed for the transient-MS experiments have been described in detail elsewhere [16,17]. Transient experiments were carried out by switching the feed composition (30 ml/min (STP)) to the reactor with the use of chromatographic valves. Responses of reactants and products were continuously analyzed and recorded employing an online mass spectrometer (Fisons, SXP Elite 300H).

FT-IR experiments were conducted employing a Nicolet 740 spectrometer, following procedures which have been described elsewhere [16–19]. Adsorption of acrolein and acrylic acid on the catalyst surface was achieved by injection of 1 μl of the corresponding liquid to a He flow, which then passed to the DRIFT cell through the catalyst bed.

3. Results

3.1. Interaction of NO with reduced and propylene-pretreated catalyst surfaces

The interaction of NO with H_2-reduced and propylene-pretreated Rh/TiO_2 catalyst surfaces was investigated at 250 °C, employing the transient-MS technique. Typical results obtained from the reduced catalyst are shown in Fig. 1A, where the transient responses of NO, N_2, N_2O and Ar recorded after the switch, He → 0.25% NO/Ar/He, are presented. It is observed that dinitrogen appears first, immediately after the switch, and reaches a plateau. After about 2 minutes-on-stream, the yield of N_2 abruptly decreases and NO starts evolving at the effluent of the reactor. This is accompanied by the formation of N_2O, which peaks at ca. 3.2 minutes-on-stream and then gradually decreases. After 10 minutes-on-stream, the response of NO reaches its initial value in the feed, indicating that all irreversible adsorption and reaction processes have ceased (Fig. 1A).

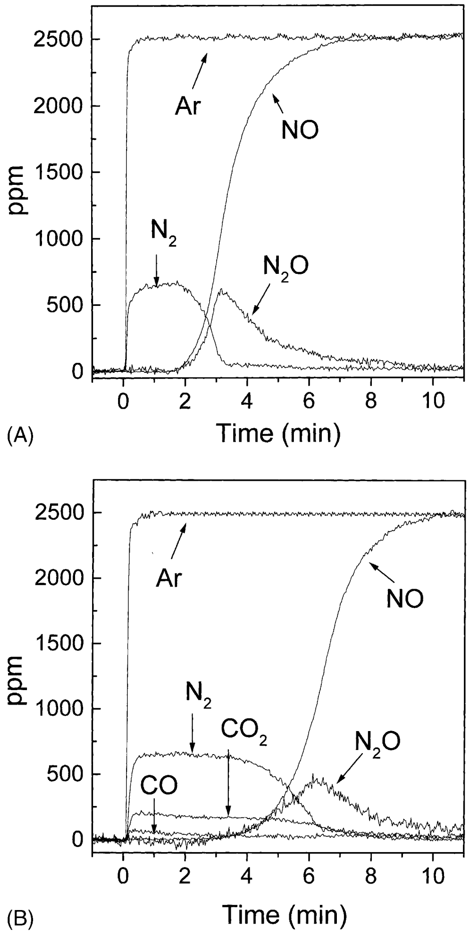

Fig. 1. Transient responses of gas phase NO, N_2, N_2O, CO_2, CO and Ar obtained at 250 °C following interaction of 0.25% NO/Ar/He with: (A) the catalyst previously reduced in situ with flowing 20% H_2/He at 350 °C for 1 h; and (B) the reduced catalyst previously treated with 0.35% C_3H_6/He at the same temperature for 15 min.

Table 1
Amounts of N_2, N_2O, CO and CO_2 formed following interaction of 0.25% NO/Ar/He with H_2-reduced and propylene-pretreated Rh/TiO_2 at 250 °C

Pretreatment	Amount of species formed (μmol/g_{cat})			
	N_2	N_2O	CO	CO_2
H_2 reduction at 300 °C for 1 h	16.1	12.8	–	–
0.35% C_3H_6/He at 250 °C for 15 min	29.9	13.2	3.2	7.9

Similar results obtained following interaction of NO with the reduced catalyst previously treated with 0.35% C_3H_6 for 15 min are shown in Fig. 1B. It is observed that the formation of N_2 takes place for almost 6 minutes-on-stream, a time period which is much longer than that observed over the H_2-reduced surface (compare with Fig. 1A). Formation of N_2 is accompanied by the production of CO_2 and lower amounts of CO in the gas phase, and it ceases when production of CO_x stops. When this happens, NO and N_2O appear in the gas phase and their responses vary with time-on-stream in a way similar to that observed over the H_2-reduced catalyst. The amounts of N_2, N_2O, CO and CO_2 formed during the above experiments are listed in Table 1.

FT-IR results obtained under conditions similar to those used in the transient-MS experiments of Fig. 1B are presented in Fig. 2. It is observed that interaction of 0.35% C_3H_6/He with the H_2-reduced catalyst results in the immediate formation of bands at 2020 and 1850–1800 cm^{-1} (trace a), attributed to linear and bridge-bonded CO on rhodium [16,17]. Increasing time of exposure to 5 min results in an increase of the intensity of both bands and in the appearance of a low frequency shoulder of the Rh^0–CO band, located at ca. 1980 cm^{-1} (trace b). Prolonged exposure to propylene leads to a progressive decrease of the intensities of the carbonyl bands and to the formation of additional, weak features at ca. 3000 and 1525/1445 cm^{-1}. As will be discussed below, these bands are due to CH_x and carboxylate (–COO^-) species, respectively.

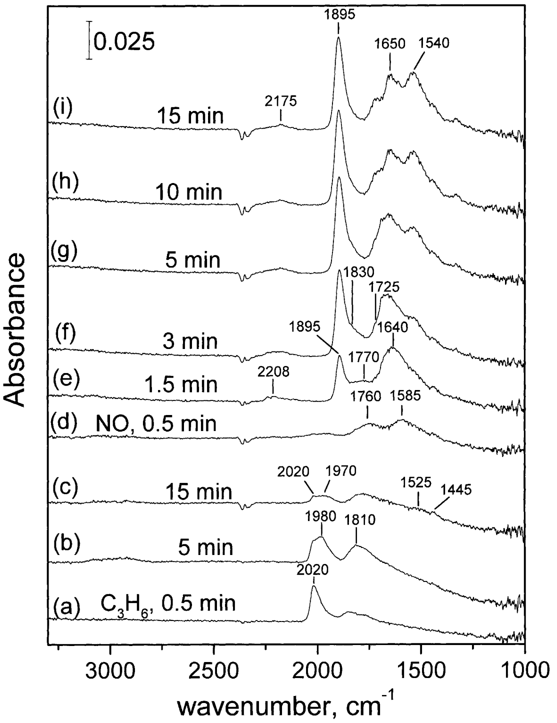

Fig. 2. FT-IR spectra obtained after interaction of the reduced catalyst with 0.35% C_3H_6/He at 250 °C for 15 min (traces a–c) and subsequent exposure to 0.25% NO/He (traces d–i).

Purging with He for 5 min and subsequent switch of the feed to 0.25% NO/He leads to the disappearance of bands due to adsorbed CO in less than 0.5 minutes-on-stream (Fig. 2, trace d), which is accompanied by the development of bands at 1760–1770 cm^{-1}, attributed to a negatively charged species adsorbed on rhodium (Rh–NO^-), and at 1585 cm^{-1}, attributed to nitrates adsorbed on the support [16,17]. Prolonged exposure to NO results in the disappearance of the band due to Rh–NO^-, after ca. 5 minutes-on-stream, and in the progressive development of an intense band at 1895 cm^{-1}, attributed to a positively charged Rh–NO^+ species [16,17]. When the intensity of the 1770 cm^{-1} band decreases and the 1895 cm^{-1} band develops, additional bands are observed at 1830 and 1725 cm^{-1} (Fig. 2, trace f), attributed to a dinitrosyl complex [$Rh(NO)_2$]. Further exposure to NO results in the dominance of bands due to Rh–NO^+ species (1895 cm^{-1}), and of bands

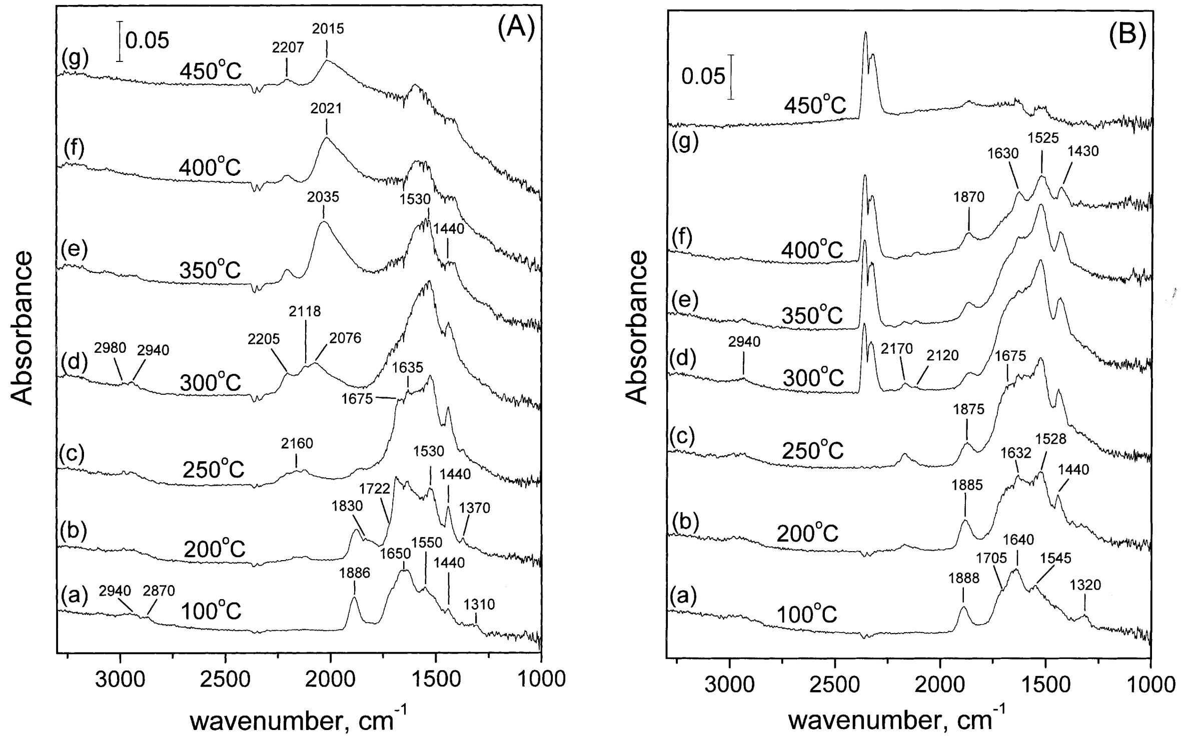

Fig. 3. FT-IR spectra recorded following interaction of the reduced catalyst with the reaction mixture at 100 °C and subsequent stepwise heating to 450 °C. Feed compositions: (A) 1000 ppm NO, 3500 ppm C_3H_6; (B) 1000 ppm NO, 3500 ppm C_3H_6, 5% O_2.

due to nitrates adsorbed on the support (bands below 1700 cm^{-1} (traces g–i). In addition to the bands mentioned above, weak bands are also observable at ca. 2210 cm^{-1}, attributed to isocyanate (–NCO) species associated with the metal and/or the support [16–19].

3.2. Investigation of surface species formed under reaction conditions

The nature and relative population of the surface species formed under reaction conditions was investigated by employing FT-IR spectroscopy. Results obtained in the temperature range 100–450 °C in the absence of oxygen in the feed are shown in Fig. 3A. All spectra were recorded in situ under steady-state reaction conditions. It is observed that interaction of the catalyst surface with the NO+C_3H_6 mixture at 100 °C (trace a) results in the appearance of bands at 1886, 1650 (broad), 1550, 1440 and 1310 cm^{-1}. The presence of the band at 1886 cm^{-1} due to Rh–NO^+ species indicates that the catalytic surface is partially oxidized by oxygen adatoms originating from dissociative adsorption of NO. At this temperature, adsorbed oxygen atoms cannot be removed from the catalyst surface due to the inability of C_3H_6 to activate the reaction.

Increasing temperature to 200 °C and above, results in significant changes of the spectrum (traces b–d). The intensity of the Rh–NO^+ band decreases with increasing temperature and disappears at 250–300 °C. This is accompanied by the appearance and growth of bands at higher frequencies, which have been previously attributed to Rh^0–CO (2076 cm^{-1}), $Rh^{\delta+}$–CO (2118 cm^{-1}), Rh–NCO (2160 cm^{-1}) and TiO_2–NCO (2205 cm^{-1}) species [16–19]. In addition, at temperature above 200 °C, several new bands develop in the region of 1700–1400 cm^{-1}. The intensity of these bands decreases with increasing temperature and the only one that observed above 350 °C are those located at 1530 and 1440 cm^{-1}. The origin and nature of these species will be discussed in detail below.

The corresponding spectra obtained in the presence of 5% O_2 in the feed are shown in Fig. 3B. It is observed that at temperatures up to 250 °C (traces a–c), the spectra are dominated by bands below $1700\,cm^{-1}$, similar to those obtained in the absence of oxygen, and by bands at 1888–1875 ($Rh–NO^+$) and $2170\,cm^{-1}$. At temperatures above 300 °C (traces d–g) oxidation of propylene takes place, as evidenced by the appearance of a doublet in the region of $2400–2300\,cm^{-1}$, attributed to gas-phase CO_2. It is interesting to note that the $Rh–NO^+$ species ($1888–1870\,cm^{-1}$) is present under all reaction temperatures examined, indicating that rhodium is partially oxidized under the present reaction conditions.

Additional FT-IR experiments were conducted to identify the origin of the spectral features appearing in the region of $1700–1300\,cm^{-1}$, in which either $NO + C_3H_6$ or isotopically labeled $^{15}NO + C_3H_6$ reaction mixtures were used. Results obtained at 250 °C (not presented) showed that the positions of these bands did not exhibit a measurable isotopic shift upon substituting NO with ^{15}NO. This observation does not lead to a safe conclusion regarding the nature of these species, due to the broadness and overlapping of the corresponding bands. However, it is highly probable that the IR bands observed in the spectral range of $1700–1350\,cm^{-1}$ are due to species which do not contain nitrogen atoms in their structure. Such species, of the general form of $C_xH_yO_z$, could be formed on the catalyst surface by partial oxidation of propylene. In order to examine this possibility, separate experiments of adsorption/thermal decomposition of acrolein and acrylic acid on Rh/TiO_2 catalyst were also performed.

3.3. Adsorption and thermal decomposition of acrolein and acrylic acid over Rh/TiO_2

The FT-IR spectrum obtained following adsorption of acrolein (CH_2=CH–CHO) at ambient temperature is shown in Fig. 4A (trace a). It is characterized by

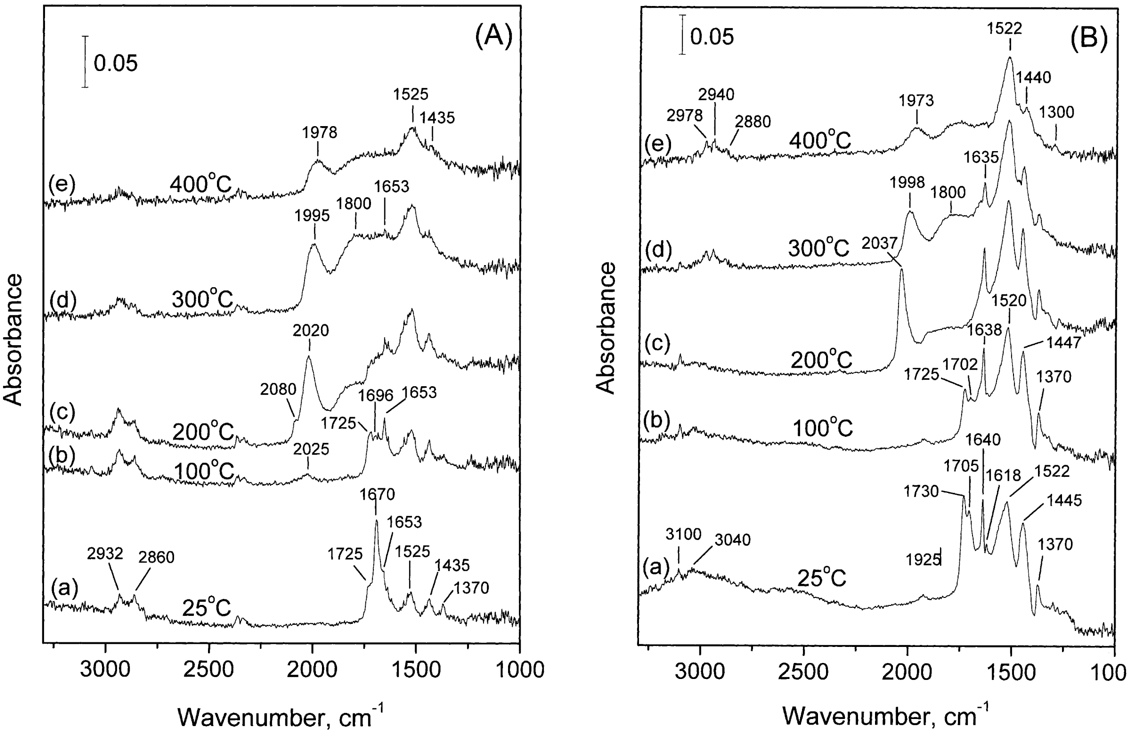

Fig. 4. FT-IR spectra obtained following adsorption of (A) acrolein and (B) acrylic acid at 25 °C and subsequent stepwise heating at 100, 200, 300 and 400 °C under He flow.

bands attributable to associatively adsorbed acrolein, located at 2932/2860 cm^{-1} [ν(C–H)], 1670 cm^{-1} [ν(C=O)], 1653 cm^{-1} (sh) [ν(C=C)], and 1370 cm^{-1} [δ_{ip}(CH)] and by bands at 1525 and 1435 cm^{-1} due to the ν_{as}(COO$^-$) and the ν_s(COO$^-$) vibrations of surface acrylate (CH_2=CH–COO$^-$) species [15,21–25].

Increasing the temperature to 100 °C (trace b) results in a significant decrease of the intensity of the 1670 cm^{-1} and in the resolution of bands at 1725 and 1696 cm^{-1}. The latter two bands may be attributed to adsorbed ketene (CH_2=C=O), originating from thermal decomposition of acrolein [22,23]. The appearance of an additional band at 2025 cm^{-1} may be safely assigned to carbon monoxide linearly bonded on reduced rhodium sites [16,17], originating from decarbonylation of acrolein and/or decomposition of ketene.

The intensity of the Rh^0–CO band increases with increasing temperature to 200 °C (trace c) and is accompanied by the development of bands at 2080 cm^{-1} and ca. 1800 cm^{-1} (broad), attributed to gem-dicarbonyl (ν_{sym}) and bridge-bonded CO on rhodium, respectively [16,17]. Further increase of temperature at 300 and 400 °C results in a progressive decrease of the carbonyl bands (traces d–e) and in a shift of the Rh^0–CO band from 2025 cm^{-1} at 100 °C to 1978 cm^{-1} at 400 °C. This shift can be attributed to the existence of hydrogen atoms and/or hydrocarbon species [15], also resulting from acrolein decomposition.

Formation of carboxylate species is enhanced by heat treatment, as evidenced by the increase of the intensity of the bands at 1525 and 1435 cm^{-1} (Fig. 4A, traces a–e). These species are very stable and were not removed from the surface even after flushing with He at 400 °C for 10 min. It should be noted here that oxidation of acrolein occurs under anaerobic conditions, so the above reactions must involve lattice oxygen of the support. This is reasonable since TiO_2 may be easily reduced at elevated temperatures, forming TiO_{2-x} species.

Adsorption and thermal decomposition of acrolein has been also examined over the unmetallized TiO_2 support. The FT-IR spectra obtained (not shown) were very similar to those presented in Fig. 4A, with the exception that the carbonyl bands at ca. 2000 cm^{-1} were absent. This provides strong evidence that adsorption and thermal decomposition of acrolein occurs on the TiO_2 support.

The FT-IR spectra obtained following adsorption and thermal decomposition of acrylic acid (Fig. 4B) are very similar to those observed for acrolein (compare with Fig. 1A). The spectrum obtained at 25 °C (trace a) is characterized by bands attributed to the vibrations of ν(C–H) at 3100–2800 cm^{-1}, ν(C=O) at 1730 cm^{-1}, ν(C=C) at 1640 cm^{-1}, ν_{as}(COO$^-$) and ν_s(COO$^-$) at 1522 and 1445 cm^{-1}, respectively, and δ_{ip}(CH) at 1370 cm^{-1}. Heating at 100 °C results in the appearance of bands at 1725 and 1702 cm^{-1} (trace b) which, as in the case of acrolein decomposition, may be attributed to the formation of adsorbed ketene species. Thermal treatment at higher temperatures (traces c–e) results in the development of bands due to adsorbed CO species at 2037 cm^{-1} (linear) and ca. 1800 cm^{-1} (bridge-bonded). As in the case of acrolein, at 400 °C the spectrum is dominated by bands due to COO$^-$ species.

4. Discussion

4.1. Chemistry of interaction of NO with Rh surfaces

Results presented in Figs. 1 and 2 are qualitatively similar to those obtained following interaction of NO with H_2-reduced and CO-pretreated 0.5% Rh/TiO_2 catalytic surfaces, at the same conditions [16], and can be explained in a similar manner: nitrogen oxide adsorbs on reduced rhodium sites in the form of negatively charged species, which absorbs at ca. 1770 cm^{-1} (Fig. 2, traces d–e). This species readily dissociates producing nitride and adsorbed oxygen atoms:

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

Formation of dinitrogen in the gas phase, which is observed during the first minutes after interaction of NO with the H_2-reduced (Fig. 1A) and the propylene-pretreated (Fig. 1B) catalyst, occurs via associative desorption of nitrides:

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

Oxygen atoms formed via Eq. (1) accumulate on the catalyst surface, resulting in a progressive oxidation of the active sites and, concomitantly, in a progressive decrease of the yield of N_2. When Rh^0 sites become less available, NO starts appearing at the exit of the reactor (Fig. 1A and B). Under these conditions, the formation of the dinitrosyl complex is favored [16,17], as evidenced by the appearance of the bands at 1830 and 1725 cm^{-1} (Fig. 2, trace f), resulting in the production of N_2O in the gas phase. Formation of nitrous oxide also requires the presence of adjacent reduced rhodium sites [16,17]:

$$\mathrm{Rh(NO)_2 + Rh^0 + NO} \rightarrow \mathrm{Rh{-}NO^+ + Rh{-}O + N_2O_{(g)}} \qquad (3)$$

Further accumulation of atomic oxygen results in complete "poisoning" of the catalyst surface. Under these conditions, irreversible adsorption and reaction processes stop, the Rh surface is covered by the "inactive" Rh–NO$^+$ species (Fig. 2, traces h–i) and the concentration of NO at the effluent of the reactor reaches that in the feed (Fig. 1A and B).

Comparison of Fig. 1A and B shows that the only difference in the transient responses of N_2, N_2O and NO is the quantity and time period for the formation of N_2 which is almost double over the propylene-pretreated sample (Table 1) and, as discussed above, is associated with the availability of Rh^0 sites. It is reasonable to suggest that this difference is due to the scavenging of adsorbed oxygen atoms, produced by NO dissociation, by preadsorbed propylene. In fact, simple calculations, using the results of Table 1, show that 30.1 μmol/g of atomic oxygen are removed from the catalyst surface in the form of CO and CO_2 (and H_2O) (Fig. 1B). This would result in the production of 15.1 μmol/g$_{cat}$ of $N_{2(g)}$, in addition to the corresponding amounts formed over the H_2-reduced catalyst. This value is in well agreement with that of 13.8 μmol/g$_{cat}$, which results from the difference of the amount of $N_{2(g)}$ produced following interaction of NO with the propylene-pretreated (29.9 μmol/g$_{cat}$) and the H_2-reduced (16.1 μmol/g$_{cat}$) catalyst (Table 1). This result provides evidence that the role of propylene in the SCR of NO is to remove adsorbed oxygen, thus regenerating the catalytically active Rh^0 sites. The reaction steps of this surface process are discussed in the following.

4.2. Reduction of NO by propylene in the absence of oxygen in the feed

Comparison of the FT-IR spectra obtained under reaction conditions, in the absence of oxygen in the feed (Fig. 3A), with those obtained following adsorption and thermal treatment of acrolein and acrylic acid (Fig. 4) shows many similarities. In particular, the development of the bands due to Rh^0–CO and of the bands below 1700 cm^{-1}, observed under reaction conditions, can be attributed to formation and subsequent decomposition of products of partial oxidation of adsorbed propene. The first step for these reactions is adsorption of propylene on the catalyst surface. Propylene adsorbs on metal and oxide surfaces forming π-allyl complexes [25]:

$$\mathrm{CH_3{-}CH{=}CH_2} \rightarrow \mathrm{CH_2 \cdots CH \cdots CH_2\,(ads) + H\,(ads)} \qquad (4)$$

Subsequent interaction with oxygen leads to partial oxidation and formation of acrolein:

$$\mathrm{CH_2 \cdots CH \cdots CH_2\,(ads) + O} \rightarrow \mathrm{CH_2{=}CH{-}CHO\,(ads)} \qquad (5)$$

Further oxidation of acrolein leads to the formation of fragments such as COO$^-$ and CH_x, with intermediate formation of acrylate-type species, in a way which has been described in detail above. During these steps, decarbonylation of the surface species occurs, which is evidenced by the presence of adsorbed CO species, at temperatures above 250 °C (Fig. 3A, traces c–g). The fact that the latter species are adsorbed on rhodium, mainly in the form of Rh^0–CO, indicates that the oxidation steps probably occur on (or in the vicinity of) oxidized Rh–O sites. However, as observed in Fig. 2 (traces a–c), adsorption of propylene and subsequent CO extraction also takes place in the absence of an oxidant such as NO or O_2 in the gas phase. It is then reasonable to suggest that adsorbed propylene may also interact with lattice oxygen from TiO_2 and then undergo similar oxidation steps.

Separate catalytic performance experiments (not presented) showed that the Rh/TiO_2 catalyst catalyzes direct reduction of NO by propylene in the absence of O_2 in the feed. This result suggests that, at least under the present conditions, NO_2 does not participate in the reduction of NO as an intermediate as proposed by other authors (e.g. [14]). Regarding the role of surface isocyanates, these species are present on the catalyst surface at temperatures above 250 °C (Fig. 3A). According to our previous findings, these species are formed by the reaction between adsorbed

CO and nitride species on reduced rhodium surfaces [17] and spillover to the support [19]:

$$Rh^0\text{–}CO + Rh\text{–}N \leftrightarrow Rh\text{–}NCO \qquad (6)$$

Detailed studies of the reactivity of these species [18] showed that isocyanates react with NO to yield N_2O, thus providing an alternative route for the production of nitrous oxide:

$$Rh\text{–}NCO + NO \rightarrow Rh + N_2O + CO \qquad (7)$$

4.3. Reduction of NO by propylene in the presence of oxygen in the feed

Comparison of the FT-IR spectra obtained under reaction conditions in the absence (Fig. 3A) and presence of oxygen in the feed (Fig. 3B), shows that the general appearance and behavior of the bands below 1700 cm^{-1} is similar. This similarity indicates that the activation and reaction of propylene proceeds via the same steps irrespective the type of oxidant employed (NO or O_2). The only major difference is that, in the presence of oxygen, an additional band appears at 1630 cm^{-1} at temperatures above 350 °C (Fig. 3B, traces e–f), which is attributable to nitrate species on the support [17]. This species dominates under conditions where production of NO_2 takes place in the gas phase and could be tentatively related to its formation.

In the presence of oxygen in the feed (Fig. 3B), the catalyst surface is partially oxidized, as indicated by the presence of $Rh\text{–}NO^+$ and the absence of Rh^0–CO species. This implies that the reduced sites produced by interaction of propylene with Rh–O are competitively reoxidized by dissociative adsorption of gas phase oxygen. As a result, the catalyst surface is partially oxidized and, concomitantly, dissociative adsorption of NO is hindered. This results in the lower activity of Rh/TiO_2 catalyst for the SCR of NO by propylene in the presence of oxygen, which, as discussed above, depends strongly on the availability of reduced Rh^0 sites on the catalyst surface. This is in agreement with the findings of Burch et al. [4,5], who studied the same reaction over Pt catalysts. On oxidized surfaces, most of the nitrogen monoxide adsorbs and desorbs without dissociation. This can allow NO adsorption, in the form of the catalytically inactive $Rh\text{–}NO^+$ species (Fig. 3B), but it is not sufficient for its dissociation.

Results of the present study (not presented) show that the activity for the SCR of NO goes through a maximum at 300–320 °C. This maximum can be explained in a way similar to that proposed for Pt catalysts [4–6]. On the metallic sites, decomposition of NO competes with dissociation of O_2. The temperature at which the maximum NO reduction is reached is determined by the relative activation energies of NO versus O_2 dissociation and propene combustion. The peak in activity results because at the peak there is a balance between the carbonaceous species removal rate and surface oxidation of Rh [4–6].

5. Conclusions

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

1. SCR of nitrogen monoxide by propylene proceeds over Rh/TiO_2 catalysts without direct interaction between C_3H_6 and NO: formation of dinitrogen in the gas phase involves dissociative adsorption of NO on reduced Rh^0 sites, with intermediate formation of $Rh\text{–}NO^-$ species, while propylene acts as an oxygen atom scavenger thus regenerating the catalytically active Rh^0 sites.
2. Oxidation of propylene and removal of atomic oxygen does not depend on the nature of the oxidant (NO or O_2) and proceeds via intermediate formation of acrolein and acrylate species, which eventually decompose to yield CO, and carboxylates on the catalyst surface.
3. The low activity observed in the presence of oxygen in the feed is due to competition between dissociative adsorption of NO and O_2, both of which take place on the catalytically active Rh^0 sites.
4. Isocyanate species may act as an intermediate providing an alternative route for the production of N_2O. In contrast, there is no evidence that NO_2 participates in the reaction as an active intermediate.

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