NO reduction by C_3H_6 and O_2 over supported noble metals Part I. Role of the support on the nature of NO_x adspecies and their relationship with the catalytic behaviour

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

The reactivity in NO reduction by C_3H_6 and O_2 of three catalysts based on Pt supported on alumina, titania and titania-alumina is studied and compared with the nature and stability of NO_x adspecies in these catalysts as determined by NO thermodesorption studies and in situ diffuse reflectance infrared (DRIFT) experiments. A relationship between activity of the catalyst and amount of weakly and reversibly coordinated NO species (suggested to be NO reversibly coordinated to surface oxygens generated by spillover on the noble metal, but stabilized by support sites) is indicated. It is also shown that the catalytic activity depends in part on the rate of transformation (in the presence of gaseous O_2) of this weakly coordinated NO_x species to species which decompose at higher temperatures (above 300 °C) and with which the formation of NO_2 during catalytic tests is associated. The catalyst based on titania-alumina shows high selectivity in NO reduction together with good activity and the widest range of temperature of maximum activity, probably due to the coexistence of nanodomains of the two oxides on the surface.
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1. Introduction

The efficient conversion of NO_x to N_2 in the presence of O_2 from lean-burn gasoline or diesel engines is still an intriguing question [1–5]. The approach based on the concept of NO_x storage-reduction catalysts [6] is the most technically feasible for light-duty engines, but there are drawbacks related to engine management and sensitivity to deactivation by sulphur. The use of ammonia, generated by urea or other chemical precursors, as the selective reducing agent for NO_x is also a technically feasible solution, but mainly for heavy-duty diesel vehicles for the necessity of multiple (typically five) catalytic beds and an extra tank on the vehicle. Open question is also the environmental impact due to ammonia slip and possible formation of harmful byproducts in traces. Direct reduction of NO_x by hydrocarbons in the presence of O_2 (hereinafter indicated as HC/O_2) would be a desirable solution if the catalyst performances can be improved (wider temperature range of activity and longer stability with time [7]).

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The catalysts for direct reduction of NO_x by HC/O_2 can be classified into two classes: (i) transition metal containing zeolites or oxides which show good performances, but only at high temperatures and with reaction rates too low for practical use and (ii) supported noble metals which show sufficient activity, but only in too restricted reaction temperature windows [7]. Therefore, understanding the reasons for the narrow reaction temperature window [8] and finding possible solutions to make it wider [9] are topics of relevant interest. This requires a better understanding of the reaction mechanism and of the nature of surface species [7]. The work presented here discuss the characteristics of NO_x adspecies as a function of the nature of the support in Pt-based catalysts to contribute to identify their relationship with the catalytic behavior in NO reduction by HC/O_2. Part II of this work will report an analysis of the reaction mechanism of NO reduction and its dependence on the nature of the support.

2. Experimental

2.1. Catalyst synthesis

The supports for the noble metal were all prepared by the sol–gel method. Ti-isopropoxide and/or tri-*sec*-butoxide were solubilized in absolute ethanol and then a solution of water, ethanol and acetic acid (1:3:4 ratio) was added slowly drop-by-drop under continuous stirring up to complete formation of a gel which was then aged at RT overnight. After filtration and washing, the solid was dried at 80 °C under vacuum, homogenised and then calcined up to 550 °C (temperature ramp of 2 °C/min). The noble metal (1 wt.% of Pt) was then added by incipient wet impregnation using a K_2PtCl_4 solution in distilled water. After drying, the catalyst was washed, calcined at 550 °C and activated by reduction at 350 °C (2 h)

using a $20\% H_2/He$ flow followed by RT passivation in air. The samples were characterized by X-ray diffraction (XRD) to check crystalline phases, atomic adsorption (AA) to determine Pt content, BET surface area and H_2 chemisorption at room temperature (using a Micromeritics ASAP 2000 analyser) to determine metal dispersion assuming a chemisorption stoichiometry, H:Pt = 1. A summary of the characteristics of the samples prepared is reported in Table 1.

2.2. Catalytic tests

The catalytic behaviour of the samples listed in Table 1 was determined using a quartz fixed bed reactor loaded with 0.1 g catalyst (40–60 mesh). The inlet and outlet reactor compositions were monitored on-line by a mass quadrupole apparatus and a GC apparatus with thermoconducibility detector. The mass intensity data were corrected to account for mass overlapping. The feed composition was 0.1% NO, 0.1% C_3H_6, 5% O_2 and 94.8% helium. The space-velocity was $60,000 \, h^{-1}$. Tests were made at increasing reaction temperature. The reactor was held at each temperature until the conversion reached a constant value. The reproducibility of the catalytic behaviour was checked by decreasing the temperature from the maximum to the lowest value; no hysteresis phenomena were observed.

2.3. Temperature programmed measurements

Temperature programmed desorption (TPD) tests in an inert flow (helium) after NO adsorption at 100 °C (NO-TPD) or temperature programmed surface reaction tests after NO adsorption at 100 °C and linear increase of the temperature in the presence of a flow containing 2% oxygen in helium (NO-TPSR/O_2) were carried out in a home made apparatus. The formation of NO, N_2, NO_2 and N_2O was monitored with a mass

Table 1
Characteristics of the samples prepared

Samples	Composition	Pt (wt.%; AA)	Phase (XRD)	BET surface area (m^2/g)	Pt dispersion (H_2 chemisorption, %)
Pt1-Al	Pt on alumina	0.98	γ-Al_2O_3	76	16
Pt1-Ti	Pt on titania	1.04	TiO_2 anatase	58	13
Pt1/Ti-Al$_{20}$	Pt on TiO_2-Al_2O_3 (20 wt.% Al_2O_3)	1.02	TiO_2 anatase	85	14

quadrupole detector. The linear increase of temperature was $10\,°C/min$ (100–600 °C range). NO preadsorption (up to saturation) in both the NO-TPD and NO-TPSR/O_2 tests was made using a flow of 0.1% $NO + x\%$ O_2 in helium, where x varied in the 0–5% range.

2.4. In situ diffuse reflectance infrared (DRIFT) studies

In situ diffuse reflectance infrared (DRIFT) studies were made using an environmental diffuse reflectance chamber mounted on a Bruker Equinox 55 FT-IR spectrometer (MCT detector). The catalyst pretreatment was: (a) 1 h calcination in 20% O_2 at 500 °C to clean the surface, (b) 1 h reduction at 350 °C with 20% H_2, (c) 1 h reoxidation in mild conditions at 200 °C with 5% O_2. Argon was used as the carrier gas. Two different types of in situ DRIFT studies were carried out: (1) as a function of time-on-stream under isothermal conditions and constant flow of NO in helium or $NO+O_2$ in helium, and (2) temperature programmed desorption experiments (100–500 °C; 10 °C/min) with argon or argon/oxygen after NO, NO/O_2 or NO_2 adsorption at 100 °C.

3. Results

3.1. Catalytic activity

Reported in Table 2 is the catalytic behaviour of the three investigated catalysts in NO reduction by propene in the presence of O_2. The amount of Pt in each catalyst was 1 wt.%

1. *Pt1-Al*: Pt supported on alumina which can be considered a model system for current three-way catalysts and a reference to compare results with published data.
2. *Pt1-Ti*: Pt supported on titania in order to analyze the effect of an alternative support having semiconductor characteristics and thus with a different electronic interaction with noble metal particles than with alumina [10].
3. *Pt1/Ti-Al$_{20}$*: Pt supported on a mixed oxide based on titania containing 20 wt.% alumina. Alumina is used as a structural promoter because it improves the surface area and stability against sintering of the materials with respect to titania alone. In addition, the anatase to rutile transition in TiO_2 is shifted to higher temperatures (above 700 °C) [11].

All three supports were prepared using the same sol–gel type methodology in order to avoid the typical impurities present in commercial oxides.

The behaviour of Pt1-Al compares well with that reported previously [1,7]. There is a sharp maximum in NO conversion to N_2 and N_2O centered at around 250 °C. The maximum selectivity to N_2 is about 50%. The maximum in NO conversion corresponds to about 90–95% of propene conversion and after the maximum NO_2 starts to be detected.

Using titania as the support (Pt1-Ti) there is a shift of about 100 °C in the activity and a drastic reduction in N_2O formation with a consequent increase in the selectivity in NO conversion to N_2 to about 70%. A slightly lower maximum NO conversion is also noted. Verykios and co-workers [10,12] have also observed the higher selectivity in NO reduction with propene and O_2 using TiO_2 or W^{6+}-doped TiO_2 as supports, but using Rh as the noble metal.

Table 2
Catalytic behavior in NO reduction by propene and oxygen of Pt1-Al, Pt1-Ti and Pt1/Ti-Al$_{20}$ catalysts

Catalyst	C_3H_6		NO		NO_2	
	Temp. of 95% conv. (°C)	Max. conv. to $N_2 + N_2O$ (%)	Temp. of max. conv. (°C)	Select. to N_2 at max. conv. (%)	Temp. range for which conv. >30% (°C)	Temp. for which conv. >10% (°C)
Pt1-Al	244	57.0	240	47.7	84	269
Pt1-Ti	346	48.4	353	70.4	60	406
Pt1/Ti-Al$_{20}$	302	55.2	329	74.9	131	371

NO thermodesorption studies and in situ DRIFT experiments on Pt supported on alumina, titania and titania-alumina indicate a relationship between activity in NO reduction by propene/O_2 and amount of weakly coordinated NO species (type I) and their rate of transformation to stronger chemisorbed NO_x species (type II).

When the titania contains 20% alumina (Pt1/Ti-Al$_{20}$) as a structural promoter, the activity slightly increases as well as the maximum in NO conversion with respect to Pt1-Ti. However, N$_2$O formation remains similar and thus the selectivity to N$_2$ is slightly higher (around 75%). Lower N$_2$O emissions are important, being N$_2$O a powerful greenhouse gas.

Another interesting difference between Pt1/Ti-Al$_{20}$ and Pt1-Al or Pt1-Ti is the wider range of temperature activity. The temperature range for which the NO conversion is higher than 30% is about 60–80 °C for Pt1-Al or Pt1-Ti, while about 130 °C for Pt1/Ti-Al$_{20}$. When the reactivity data were compared with the surface area of the catalysts or the dispersion of the noble metal (see experimental part), no direct relationship could be observed.

3.2. NO thermodesorption experiments

Two types of NO thermodesorption experiments were made. In the first type (NO-TPD), NO is adsorbed at 100 °C up to saturation in the presence of variable O$_2$ contents in the feed. After a short flushing with He the NO which desorbs from the catalyst in a He flow is monitored in the 100–600 °C temperature range. In NO-TPSR/O$_2$ experiment the adsorption of NO is made as in the first case, but O$_2$ is present in the feed during thermodesorption.

Compared in Fig. 1 are the NO-TPD results (adsorption in the presence of O$_2$) with NO-TPSR/O$_2$ results (adsorption without O$_2$ in the feed) (square and circle symbol, respectively). Two desorption peaks for NO are observed, the first centered around 200–250 °C and the second centered at 350–500 °C. The second is also associated to O$_2$ desorption. The temperature of both peaks shifts to higher values in the order Pt1-Al < Pt1/Ti-Al$_{20}$ < Pt1-Ti following closely the activity order. The shift to higher temperatures is more limited for the low temperature peak (from about 180 to 250 °C) than for the higher temperature peak (from 350 to 500 °C). Furthermore, while the higher temperature peak intensity does not depend on the absence or presence of oxygen during the NO adsorption stage, the intensity of the lower temperature peak depends significantly on the O$_2$ concentration during the adsorption stage. The area of the first peak in Pt1-Al nearly halves when the O$_2$ concentration decreases from 2% as in Fig. 2 to 1%. In Pt1-Ti the intensity of
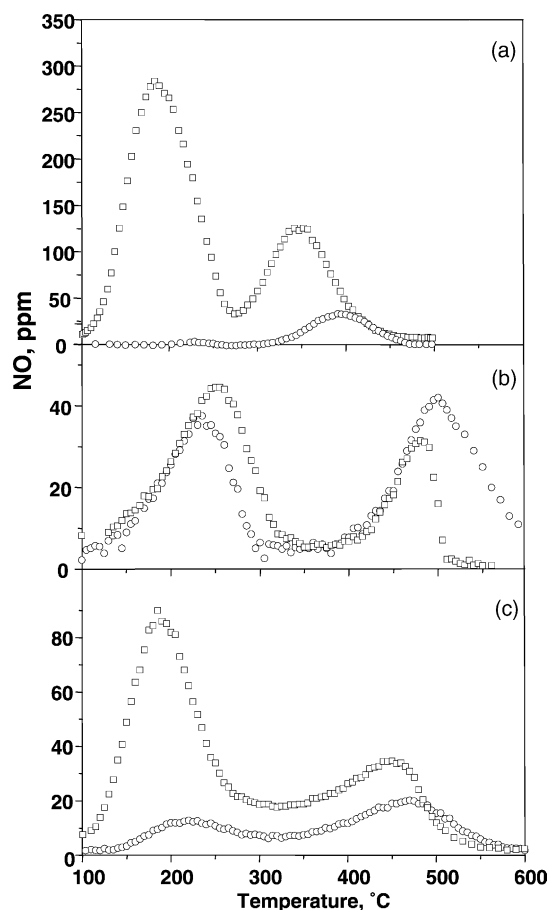

Fig. 1. NO-TPD and NO-TPSR/O$_2$ tests (see text) on Pt1-Al (a), Pt1-Ti (b) and Pt1/Ti-Al$_{20}$ (c) catalysts. (□) Adsorption: 0.1% NO, 2% O$_2$, He; desorption: 100% He. (○) Adsorption: 0.1% NO, He; desorption: 2% O$_2$, He.

this peak instead decreases only about 10–15%, while in Pt1/Ti-Al$_{20}$ about 50–60%. The intensity of this low temperature peak in NO-TPD runs follows the order of activity (the more intense in the most active Pt1-Al sample), but in NO-TPSR/O$_2$ tests the opposite trend is observed. No relevant differences are noted in terms of intensity of the higher temperature desorption peak in the three catalysts. The ratio between low and higher temperature NO desorption peaks depends on the catalyst. This ratio decreases from slightly higher than 1 in Pt1-Ti to 0.1–0.2 in Pt1-Al.

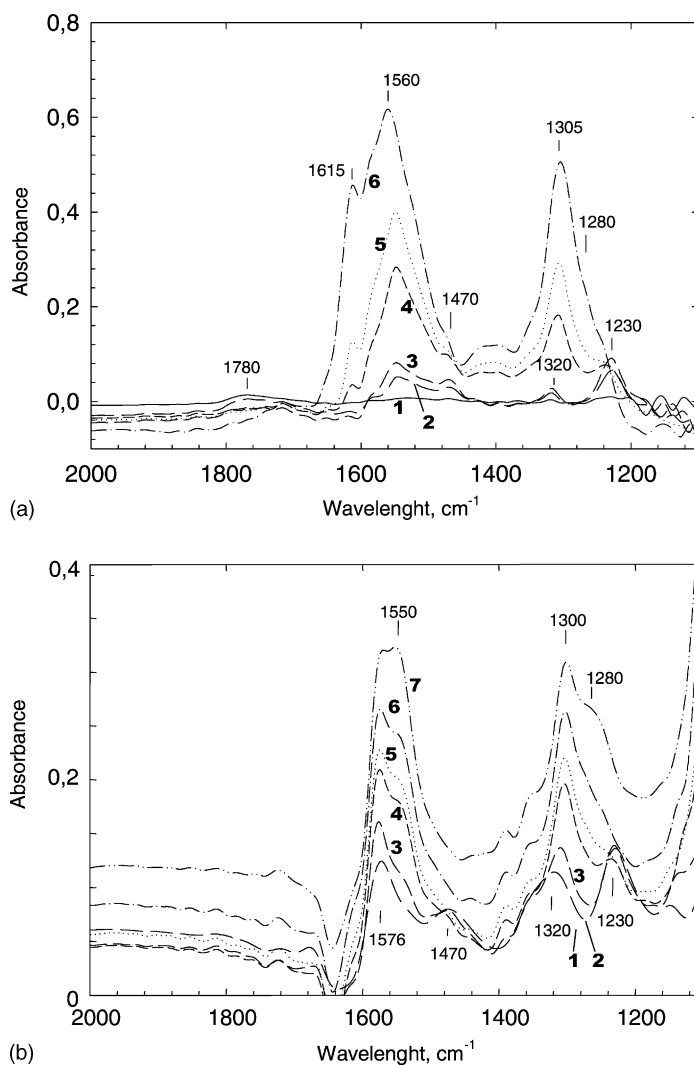Additional NO thermodesorption tests were also made changing the noble metal loading in the

Fig. 2. In situ DRIFT spectra during NO or NO + O_2 in helium interaction with Pt1-Al at 100 °C (a) or during thermodesorption in Ar flow after interaction at 100 °C with 0.1% NO + 1% O_2 in helium (b). (a) Feed composition and time: (1) base; (2) 0.2% NO, 95 min; (3) 0.2% NO, 200 min; (4) 0.2% NO + 0.8% O_2, 1 min; (5) 0.2% NO + 0.8% O_2, 10 min; (6) 0.2% NO + 0.8% O_2, 65 min. (b) Temperature of desorption: (1) 120 °C; (2) 160 °C; (3) 200 °C; (4) 240 °C; (5) 280 °C; (6) 330 °C; (7) 400 °C.

0–2.0 wt.% range or using Rh instead of Pt. Minor differences were noted, apart using the supports alone. This suggests that the desorption peaks shown in Fig. 1 are associated with sites present on the support, but the formation of these NO_x adspecies (especially those related to the low temperature desorption peak) depends on the presence of the noble metal.

3.3. In situ DRIFT studies

In situ DRIFT spectra during NO or NO + O_2 interactions with Pt1-Al at 100 °C are reported in Fig. 2a. After interaction of NO with the catalyst, a band centered at 1230 cm^{-1} immediately forms and later a broader band centered at 1576 cm^{-1} with a shoulder 1470 cm^{-1} and a band near 1320 cm^{-1} also

slowly develop. No bands in the 1700–2000 cm^{-1} region could be noted (nitrosyl species) apart from a broad and very weak band at 1780 cm^{-1} which can be assigned to partially negatively charged NO$^{\delta-}$-Pt species [13]. No further bands are observed at higher frequencies (2000–2500 cm^{-1} region) pointing out the absence of detectable coordinated species such as N$_2$O or NO$_x^{\delta+}$. The bands at 1230 cm^{-1} can be assigned to the N–O stretching mode of a negatively charged coordinated NO molecules. This species forms immediately either from NO or NO + O$_2$, but in the latter case the very fast growth of more intense bands in the 1300–1700 cm^{-1} region makes difficult its detection (Fig. 2a). For longer times-on-stream either in the presence or absence of O$_2$ more intense bands form in the 1300–1700 cm^{-1} region. The shape of this envelope of bands is similar in both cases, but the bands are more intense and grow faster in the presence of O$_2$. Bands in this region are attributed to nitrite and nitrate species. Although unequivocal assignment is not possible, the presence of coordinated nitro, M–NO$_2$ (bands at 1470 and 1320 cm^{-1}) may be tentatively identified and for longer times-on-stream mono- and bridging-nitrate, M–O–NO$_2$ and (M–O)$_2$NO, respectively (bands at 1560 and 1305 and at 1615 and 1280 cm^{-1}, respectively) [13].

The change of the spectra increasing temperature after NO+O$_2$ adsorption at 100 °C is reported in Fig. 2b. Note that in order to better evidence the changes, the spectra in Fig. 2b have different magnification. The absolute intensity of the spectra decreases with increasing temperature. The spectra are analogous to those discussed above, but above about 240 °C new bands increase at 1550 and 1280 cm^{-1} and the band at 1320 cm^{-1} shifts to 1300 cm^{-1}. A negative band near 1620 cm^{-1} due to desorption of water prevents analysis in the 1600–1650 cm^{-1} region, but possibly a band in this region is present. Note also that the temperature at which the modifications in the spectra become more evident coincides with the temperature of the maximum in activity of this catalyst.

In situ DRIFT spectra at 100 °C for Pt1-Ti catalyst as a function of time-on-stream in the presence of a flow of NO/helium or NO + O$_2$/helium are reported in Fig. 3. At the lower temperature (Fig. 4a), the interaction of NO or of NO + O$_2$ (for a shorter time) with the catalyst gives rise to the same spectrum characterized by a broad band centered at 1468 cm^{-1} plus
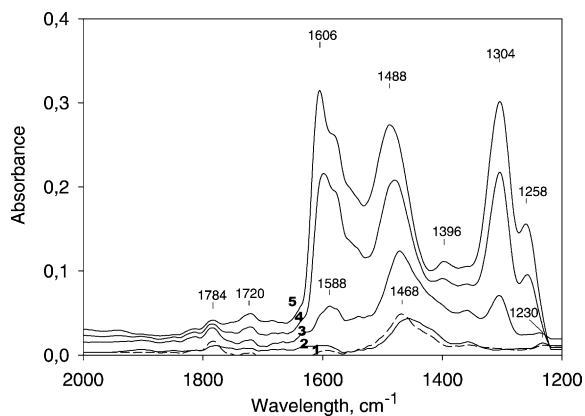

Fig. 3. In situ DRIFT spectra during NO or NO + O$_2$ in helium interaction with Pt1-Ti at 100 °C. Feed composition and time. (1) 0.5% NO, 10 min; (2) 0.5% NO + 5.0% O$_2$, 5 min; (3) 0.5% NO + 5.0% O$_2$, 30 min; (4) 0.5% NO + 5.0% O$_2$, 90 min.

a weak band centered at 1784 cm^{-1}. The latter can be assigned to NO$^{\delta-}$-Pt species, while the broad band at 1468 cm^{-1} associated also with a weak band at about 1350 cm^{-1} can be attributed to a monodentate nitrite (M–O–NO) ion (asymmetric and symmetric $\nu_{N=O}$). A weak band at 1230 cm^{-1}, similar to that discussed for Pt1-Al, can be also noted.

For longer times-on-stream, the band shifts to 1488 cm^{-1} and strong bands form centred at 1606 cm^{-1} (with a shoulder at 1550 cm^{-1}) and at 1304 cm^{-1} (with a shoulder at 1258 cm^{-1}). These bands are similar

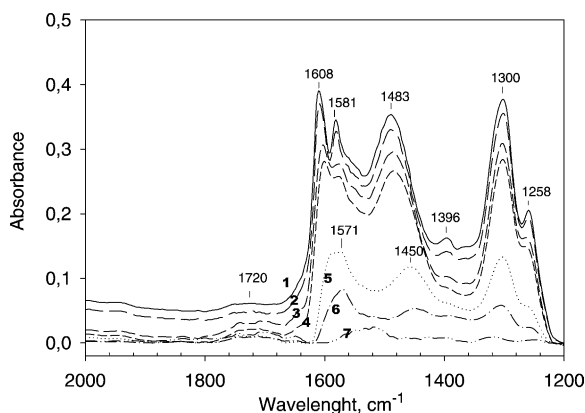Fig. 4. In situ DRIFT spectra during thermodesorption in Ar flow after interaction with Pt1-Ti at 100 °C with 0.5% NO + 5% O$_2$ in helium. Temperature of desorption. (1) 100 °C; (2) 200 °C; (3) 250 °C; (4) 300 °C; (5) 400 °C; (6) 450 °C; (7) 500 °C.

to those observed on Pt1-Al, although in the latter catalyst the band at $1560 \, cm^{-1}$ is stronger than that at $1615 \, cm^{-1}$. They can be assigned to mono- and bridging-nitrate as in the case of Pt1-Al. At higher temperature ($300\,^\circ C$) the change in the spectra with time-on-stream is similar to that observed at $100\,^\circ C$, but much shorter times (about 1/15 of those at $100\,^\circ C$) are necessary to obtain comparably intense spectra. Note that the band at $1784 \, cm^{-1}$ ($NO^{\delta-}$-Pt) is clearly present also at this higher reaction temperature.

The change in the spectrum of the NO_x adspecies on Pt1-Ti as a function of the temperature after interaction of $NO + O_2$ at $100\,^\circ C$ is reported in Fig. 4. With increasing temperature, the spectrum of the NO_x adspecies does not change significantly up to a temperature of about $300\,^\circ C$ (temperature of the start of catalytic activity in this sample; see Fig. 1), and then decreases significantly in the 300–$400\,^\circ C$ temperature range. A change in the spectrum also occurs with a relatively stronger decrease in the bands at 1608 and $1258 \, cm^{-1}$ (bridging-nitrate) and a shift in the band from 1483 to $1450 \, cm^{-1}$ due to the disappearance of coordinated nitro species. Comparison of the spectra for Pt1-Al and Pt1-Ti shows that although there are some analogies, the nature and stability of the NO_x adspecies is different. On Pt1-Ti monodentate nitrite is more abundant than on Pt1-Al and also the kinetics of formation of the nitrate species are slower. In addition, the relative stabilities of the mono- versus bridging-nitrate are opposite for the two catalysts. However, in both catalysts a change in the nature of the nitrate species was observed in coincidence with the temperature range of maximum activity in NO reduction to N_2.

Reported in Fig. 5 are the in situ DRIFT spectra for Pt1/Ti-Al$_{20}$ as a function of time-on-stream during interaction at $300\,^\circ C$ with a $NO + O_2$ in helium feed. Spectra were also recorded at lower temperature ($100\,^\circ C$), but results are not significantly different from those at $300\,^\circ C$, apart for a slower kinetic. The spectra closely resemble those obtained for Pt1-Al more than those for Pt1-Ti as would be expected based on the fact that titania is the dominant phase (80%). However, for Pt1-Al a more intense shoulder occurs at $1490 \, cm^{-1}$, in correspondence to the band at this frequency characteristic of Pt1-Ti. Furthermore, the ratio between the bands at 1604 and $1570 \, cm^{-1}$ is intermediate between those for Pt1-Al and Pt1-Ti.
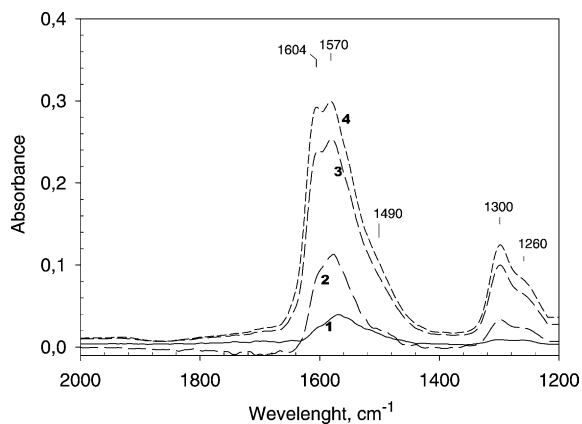

Fig. 5. In situ DRIFT spectra during $NO+O_2$ in helium interaction with Pt1/Ti-Al$_{20}$ at $300\,^\circ C$. Feed composition and time. (1) 0.5% $NO + 5.0\%\ O_2$, 1 min; (2) 0.5% $NO + 5.0\%\ O_2$, 3 min; (3) 0.5% $NO + 5.0\%\ O_2$, 10 min; (4) 0.5% $NO + 5.0\%\ O_2$, 20 min.

4. Discussion

4.1. Nature of NO_x adspecies

In NO-TPD tests (Fig. 1), the dependence of the low temperature peak on the O_2 concentration during preadsorption and the presence of the noble metal, suggests that the NO_x adspecies desorbing at low temperature may be tentatively assigned to weakly adsorbed NO_x species associated with NO coordinated to surface sites produced by spillover of oxygen on the noble metal and which reversibly dissociates forming NO as the reaction temperature increases when O_2 is absent in the feed.

The amount of these surface sites depends on the support, being higher on alumina than on titania which however shows a lower tendency to transform these weakly coordinated species to more strongly coordinated species when gas phase O_2 is present in the feed during the thermodesorption run. In fact, this low temperature peak completely disappears in the case of Pt1-Al, while it is only slightly affected in the case of Pt1-Ti. Pt1/Ti-Al$_{20}$ shows behaviour intermediate between that of Pt1-Al and Pt1-Ti. In situ DRIFT spectra (Fig. 5) confirm that the presence of 20 wt.% alumina as the structural promoter for titania alters significantly the surface properties which become intermediate between those of alumina and titania, probably due to

the coexistence of surface nanodomains of the two oxides.

In situ DRIFT experiments (Figs. 2–4) confirm also the results of the thermodesorption experiments (Fig. 1) regarding the range of stability of NO_x adspecies as well as the slower rate of transformation of nitrite (or coordinated NO_2) to nitrate on Pt1-Ti with respect to Pt1-Al. The exact nature of the species responsible for the low temperature desorption peak could not be determined by comparing the DRIFT and thermodesorption data. Probably, the extinction coefficient of this species is lower than that of the surface nitrite–nitrate species giving rise to the broad envelope in the $1200–1700\,cm^{-1}$ region. The band at $1230\,cm^{-1}$ discussed in reference to Pt1-Al and attributed to ν_{NO} of a negatively charged NO species interacting with surface oxygens could be the sign of the species responsible for the low temperature desorption peak in TPD runs, but more studies are necessary.

No or very weak bands due to nitrosyl coordinated to platinum were observed in the DRIFT experiments on Pt1-Al and Pt1-Ti, differently from previous studies, clearly indicating the presence of this type of species when metallic Pt particles are present [12]. Our results indicate that over oxidized Pt particles, reasonably present during our in situ studies, the presence of this type of species is minimal.

No correlation between surface area and area of the low or high temperature NO desorption peaks could be noted, indicating that the amount of these species is a function of the surface characteristics of the support oxide more than a function of surface area only.

4.2. Relationship between nature of NO_x adspecies and catalytic behavior

The comparison between NO thermodesorption and catalytic data suggest the following relationships:

(1) The temperature range of desorption of the species corresponding to the first lower temperature peak (attributed to NO reversibly coordinated to surface oxygens possibly generated by spillover on the noble metal) nearly coincides with the temperature range of activity of the catalysts in NO reduction by C_3H_6 in the presence of O_2.

(2) The integral area of this lower temperature peak (proportional to the amount of this species) after analogous conditions of NO adsorption in the presence of O_2 is related to the catalytic activity (the more abundant the species, the more active the catalyst).

(3) The temperature of the maximum in the higher temperature desorption peak follows the order of activity of the catalysts, but this peak (attributed to decomposition to NO and O_2 of surface nitrate adspecies) occurs in a temperature range above the range of NO selective reduction and instead coincident with the range of formation of NO_2.

(4) The rate of transformation in the presence of O_2 of the lower temperature NO_x adspecies (NO reversibly coordinated to surface oxygens) to those decomposing at higher temperature (above $300\,°C$) is faster in Pt1-Al than in Pt1/Ti-Al$_{20}$ and Pt1-Ti (compare the NO-TPSR/O_2 results), and also follows the order of formation of NO_2.

These results suggest that the catalytic performances of this series of catalyst can be put in relation with the amount of the first species desorbing NO at lower temperature (attributed to NO reversibly coordinated to surface oxygens), but the catalyst performances also depend on the tendency of this species to be transformed to more thermally stable nitrate-like surface species.

On alumina sample this low temperature NO_x adspecies is more abundant and therefore the catalyst results more active at lower temperatures, but at the same time, probably due to surface acido-base properties, this NO_x adspecies fast also transforms in the presence of oxygen to the second type of species responsible of the higher desorption peak and probably of N_2O formation. As a consequence the temperature windows of maximum activity is narrow and selectivity to N_2 low. On titania sample the rate of oxidation of the low temperature NO_x adspecies is slow (therefore, higher selectivity to N_2), but also lower the amount of these NO_x adspecies and thus activity. Using titania-alumina supports composed of surface nanodomains of the two oxides, it is possible to combine the characteristic behaviours of the two supports (higher activity of alumina and higher selectivity of titania). Furthermore, the temperature windows of maximum activity in NO reduction is higher.

Although the temperature window enlargement is still limited for practical applications, these results indicate the concept that the nature of the support and not only the noble metal and its characteristics such as dispersion is an important parameter to consider towards the goal of developing catalysts for the selective reduction of NO with hydrocarbons in the presence of O_2. The results also evidence that the nature of the support determines the amount, stability and reactivity with oxygen of surface NO_x adspecies and these aspects should be consider to fully understand the reactivity and reaction mechanism in NO_x selective reduction. It may be noted, in fact, that notwithstanding the large number of mechanistic studies [1,4,6], no clear explanation is given in literature about the sharp maximum in NO conversion of supported noble metals and the dependence of it from the nature of the support.

5. Conclusions

The analysis of the reactivity and nature of the NO_x adspecies on catalysts based on Pt supported on alumina, titania and titania-alumina suggests a relationship between activity of the catalyst in the selective reduction of NO in the presence of propene/O_2 and amount of weakly and reversibly coordinated NO species (suggested to be NO reversibly coordinated to surface oxygens generated by spillover on the noble metal, but stabilized by support sites). In situ DRIFT spectra provide little evidence about the nature of this species, being dominated by stronger bands associated with nitrito–nitrato species, although this species could be associated with a band at $1230\,cm^{-1}$ detected for the shorter times-on-stream.

The catalytic activity also depends on the rate of transformation (in the presence of O_2) of this weakly coordinated NO_x species to those decomposing at higher temperature (above $300\,°C$) and to which is associated the formation of NO_2 during the catalytic tests.

Using a titania-alumina mixed oxide as the support for Pt it is possible to combine the superior selectivity performances in NO reduction found with titania supports with good activity and a wider range of temperature of maximum activity. This derives from the probable coexistence of nanodomains of the two oxides on the surface which give rise to catalytic behaviour and surface properties intermediate between those of the two supports (higher activity of alumina and higher selectivity of titania).

Acknowledgements

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