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# The Relation between Surface State and Reactivity in the DeNO$_X$ Mechanism on Platinum-Based Catalysts

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**The selective reduction of nitrogen oxides by hydrocarbon on Pt supported on $La_2O_3$, $ZrO_2$, and a mixture of both has been studied. The supports were prepared by a sol-gel technique. Following a standard pretreatment with oxygen and water, it was found that the platinum was existing in a mixture of both oxidised and reduced forms, yet during the course of the reduction reaction, all of the metal became oxidised. A systematic study of the parameters influencing the reaction demonstrated $NO_2$ is not a reaction intermediate. The metal remains fully oxidised during the course of the reaction and the hydrocarbon is unable to reduce it; therefore the SCR proceeds without NO dissociation.** © 1999 Academic Press

*Key Words:* **selective catalytic reduction; $NO_x$; platinum; zirconia; lanthana.**

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## 1. INTRODUCTION

A predominant challenge to both industrial and academic research institutions is the selective reduction of $NO_x$ during lean exhaust conditions. Nitrogen oxides ($NO_x$), are emitted primarily from transportation and other industrial sources and contribute largely to a variety of environmental problems: the formation of acid rains and the resultant acidification of aquatic systems, ground level ozone, and general atmospheric visibility degradation. The major source of nitrogen oxides is the combustion of fossil fuels such as coal in electrical power plants or petroleum in the engines of vehicles and aeroplanes. In both cases the processes are so fast that the thermodynamic equilibrium ($CO_2 + H_2O$) is not reached. For this reason, the exhaust gases contain products of an incomplete combustion such as soot or carbon monoxide. Nitrogen oxides are also formed and among them, nitrogen monoxide, NO, accounts for 95% of all nitrogen oxide emissions.

To meet the stringent regulations imposed by the EC upon motor car manufacturers, exhaust after-treatments have become necessary. One of these is selective catalytic reduction by hydrocarbons (HC-SCR). An enormous amount of catalytic material has now been developed (1) and an appropriate choice would seem to be supported noble metal catalysts (2). A high activity is generally observed at low temperature while efficiency remains little affected by water. Although well studied, the reaction mechanism is still undergoing continuous debate in the current literature. The various theories often seem contradictory. For certain authors, the mechanism involves an NO adsorption step prior to its decomposition and the regeneration of the active site proceeds via the reduction of the adsorbed oxygen by hydrocarbon (3, 4). In another mechanism, the key step is the transformation of NO into $NO_2$, the reaction intermediate which further oxidises adsorbed organic species such as nitro, nitrite, and carbonyl in the presence of oxygen into $N_2$, $N_2O$, and $CO_2$ (5). Bamwenda *et al.* (6) have investigated the surface intermediates by FTIR and found adsorbed hydrocarbons, isocyanates, cyanides, and nitrosonium cations. They proposed the N–CO species as a reaction intermediate. Engler *et al.* have studied the SCR (7) and by varying reaction parameters such as the nature of the hydrocarbon, the HC/NO ratio coupled with diffuse reflectance FTIR results, they were able to propose a “dual-site” mechanism in which the hydrocarbon and NO are adsorbed on different sites reacting with oxygen to give adsorbed $NO_2$ and an adsorbed “oxy-hydrocarbon” which react together to produce $N_2$, $CO_2$, and $H_2O$.

Although platinum seems to be universally accepted as the most active metal, few studies report the effects of the support. Inaba *et al.* (8) observed that when supported on $Al_2O_3$, platinum is more active for the reduction of NO by propane than when supported on $SiO_2$. Burch and Watling (9) moderated these results by stating that the activity depends upon the reducing agent more than upon the support. For example, they noted the reverse result when using propene instead of propane. Another study by Bamwenda *et al.* (6) shows the important influence of the nature of the support upon catalytic activity. The alumina-based catalyst gave the highest NO conversion and therefore resultant nitrogen production.

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In this paper, we present the results of a catalyst prepared by impregnation of a support made from zirconia and lanthanum oxide either in combination or alone, prepared in each case by a sol-gel technique. A systematic study of the parameters influencing the reaction was performed in order that participation in the ongoing debate in the literature might be undertaken and to prove that the structure of the catalyst could ascertain or eliminate certain assumptions relative to the mechanism detailed in recent publications.

## 2. EXPERIMENTAL

### 2.1. Preparation of the Catalysts

The catalyst was made by impregnation of an ethanolic solution by $Pt(NH_3)_2(NO_2)_2$ of a $La_2O_3$–$ZrO_2$ support prepared in the following manner: the method comprised a simultaneous precipitation of $La(NO_3)_3$, $6H_2O$, and $ZrO(NO_3)_3$, $6H_2O$ dissolved in ethanol by oxalic acid. The solvent was then evaporated and the remaining powder dried overnight in an oven at 120°C and then calcined in air at 550°C for 3 h, with a ramp rate of 5°C $min^{-1}$. The same technique was used to prepare $La_2O_3$ or $ZrO_2$. Following impregnation of the platinum salt, the catalyst was again calcined under the same conditions but only for 1 h. The atomic absorption analysis (SCA, Solaize, France) implied a 1/1 ratio between La and Zr and a percentage inclusion of Pt equal to 1. The BET surfaces were reproducible and always comprised between 10 and 20 $m^2\ g^{-1}$. Under those conditions, an XRD pattern was not observed for $ZrO_2$, for $La_2O_3$, or for a well-defined structure between Zr and La.

The catalysts possessed of platinum dispersions measured by pulse CO chemisorption of 35% for Pt/$La_2O_3$–$ZrO_2$, 22% for Pt/$La_2O_3$, and 39% for Pt/$ZrO_2$.

### 2.2. Pretreatment and Catalytic Test Procedure

The reaction was carried out in a dynamic flow reactor using a synthetic gas mixture. The flow rates were adjusted using Tylan mass flow controllers and the effluents were analysed using IR or UV analysers from the Binos range for NO, $NO_2$, and $N_2O$ and FID chromatography for the hydrocarbons. The gas was humidified by passage through a water saturator regulated at 50°C. Before the analytical section, a Perma Pure dryer was installed to selectively remove water vapour from the gas stream. The data were collected every 10 s on a computer using “purposely written” software.

The catalyst was pretreated in a mixture of 6% $O_2$ and 12% $H_2O$ in nitrogen for 30 min. This procedure represents the so-called standard pretreatment as written in the text. The temperature was increased to 450°C with a ramp rate of 4°C $min^{-1}$ and was maintained for 30 min. The temperature was then decreased to 150°C and the reacting gas mixture introduced. The standard comprised 500 ppm NO, 220 ppm $C_3H_8$, 110 ppm $C_3H_6$, 350 ppm CO, 6% $O_2$, 10% $CO_2$, 12% $H_2O$, and the GSHV was 60.000 $h^{-1}$. For the mechanistic studies a number of the concentrations were changed. Details of these variations will be given in the text where appropriate.

The N-containing products of the reaction are $N_2$, $N_2O$, and $NO_2$. $N_2$ was not analysed; therefore, the results are expressed by the conversion of NO ($X_{NO}$) and the production of $NO_2$ ($X_{NO_2}$) and $N_2O$ ($X_{N_2O}$). The conversion of NO into $N_2$ is given by: $X_{N_2} = X_{NO}\text{-}X_{NO_2}\text{-}X_{N_2O}$. The conversion of hydrocarbon is calculated from the amount of unreacted HC in the gas phase and all are expressed as percentages (%).

### 2.3. Electron Microscopy

The electron microscopy analyses were carried out by Volvo (AB Volvo, Technological Development, Göteborg, Sweden) using a transmission electron microscope JEOL 2000 FX equipped with EDX analysis facilities. The solids were deposited upon carbon grids by evaporation of the solvent containing a suspension of the catalyst. The particle sizes were determined by computer analysis using a public software (program Image).

### 2.4. XPS

XPS spectra were recorded on a VG-ESCA III spectrometer with Al $K\alpha$ X rays as photons source (1486.6 eV). The apparatus allows *in situ* treatments under oxygen or hydrogen at 1 Atm. and up to 900°C. The power of the X-ray source was set at 100 W and the time to record all the transitions of interest was 90 min. A flood gun was used to balance the charge effects due to ion milling. The sample in the preparation chamber was systematically submitted to a calcination under 6% $O_2/N_2$ for 2 h at 450°C. Binding energies (BE) were referenced from the C(1s) peak at 284.5 eV.

Pt 4f photoemission lines were determined using a curve-fit. Binding energies corresponding to the core levels of Pt $4f_{7/2}$ and $4f_{5/2}$ proved characteristic. The energies used for the fitting procedure are reported in Table 1.

**TABLE 1**

**Binding Energies for Pt $4f_{7/2}$ and $4f_{5/2}$ for Different Platinum Compounds**

| | Pt $4f_{7/2}$ (eV) | Pt $4f_{5/2}$ (eV) |
|---|---|---|
| Pt | 71.2 | 74.6 |
| PtO | 72.3 | 75.6 |
| $PtO_2$ | 73.6 | 76.8 |

### 2.5. Temperature Programmed Reduction (TPR)

Temperature programmed reduction is a classical method for characterising supported catalysts. The analyses were performed using an apparatus of the $\chi$-sorb range commercialised by Gira. Prior to reduction, the catalyst placed in a U-shaped reactor was calcined in an air flow at 300°C with a ramp rate of 10°C $\text{min}^{-1}$ for 4 h. Then, after cooling to room temperature, the catalyst was reduced in a flow of 1% $H_2$ in argon. The temperature was programmed to increase at a constant rate of 8°C $\text{min}^{-1}$ up to 550°C. The gas composition was analysed by means of a catharometer and the data were collected on a computer.

## 3. RESULTS

### 3.1. State of the Metal after the Standard Pretreatment

For the $Pt/La_2O_3$–$ZrO_2$ sample the extent of chemisorption was ascertained by electron microscopy measurements. The EDX revealed the presence of regions containing both lanthanum and zirconium and others containing zirconium alone. The metallic particles in view were constituted singularly of platinum. The photographs showed a large number of particles having a mean diameter of 40 Å ± 4 Å. Few particles with a diameter approaching 300 Å were identified. The dispersion calculated from the proposition defined by Benson and Boudart (10), ca. 30%, was in good agreement with the value obtained from the chemisorption (35%).

Figure 1 shows the XPS spectrum of binding energies corresponding to the core levels of Pt $4f_{7/2}$ and $4f_{5/2}$ following treatment under 6% $O_2$ at 450°C. The result of the mathematical deconvolution indicated clearly that the platinum existed predominantly in the form of PtO (80%), with the remainder in the metallic form. The structure of PtO has been identified by XPS only recently; it was always thought to have been a mixture of $PtO_2$ and Pt°. There are very few reports in the literature concerning platinum oxides; however, some years ago, Hecq *et al.* secured films of oxygen–platinum compounds by reactive sputtering and investigated their structure by photo-emission (11) in order to identify electron binding energies for $Pt^{2+}$ and $Pt^{4+}$. They have categorically confirmed that a structure of PtO similar to PdO (tetragonal) does indeed exist. Our opinion is that the existing fraction of reduced platinum is not on the surface but constitutes the core of the particles since the mechanism of metal oxidation always proceeds from the surface to the core. Equally, the presence of an isolated region of reduced platinum upon a surface of oxidised platinum is highly improbable. More likely is that the particle is constituted of a core of reduced platinum recovered by a thick layer of PtO.

A further characterisation of the oxidised state of the catalysts was carried out using TPR, as described by Figs. 2a, 2b, and 2c for $Pt/ZrO_2$, $Pt/La_2O_3$, and $Pt/La_2O_3$–$ZrO_2$ respectively. The quantities of platinum reduced, according to the reaction between platinum dioxide and hydrogen such as: $PtO_2 + 2H_2 \rightarrow Pt + 2H_2O$, are presented in Table 2. The reduction profile of $Pt/ZrO_2$ is represented by a single peak with a maximum at 207°C. The amount of hydrogen consumed is equal to that necessary to fully reduce the platinum dioxide, within experimental accuracy. Above 400°C, a reduction peak appears which could be attributed to the reduction of some carbonates formed during storage. The reduction of $Pt/La_2O_3$ is a two-step process with maxima at 308 and 347°C. The amount of hydrogen consumed also corresponds to the quantity required for total reduction of platinum dioxide into the metallic form. Therefore, by way of explaining the presence of the second peak, no partial reduction of the support could be involved as proves the case when palladium is used instead of platinum (12). In our

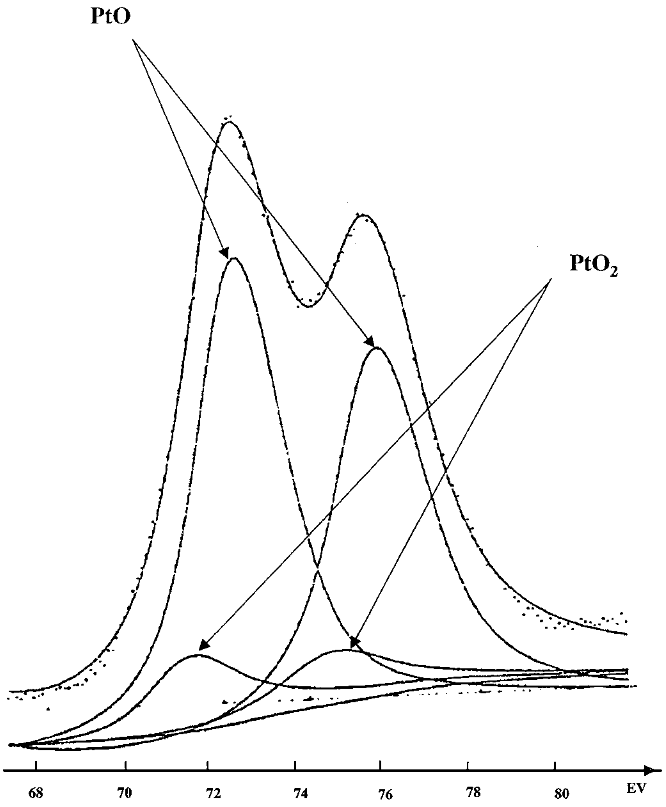

**FIG. 1.** XPS spectrum at the 4f level of $Pt/La_2O_3$–$ZrO_2$ calcined at 550°C.

**TABLE 2**

**Amount of Platinum Reduced during TPR Experiments**

| Catalyst | Amount of Pt ($\mu$mol) | Amount of $H_2$ ($\mu$mol) | H/Pt |
|---|---|---|---|
| $Pt/ZrO_2$ | 15.4 | 14.3 | 0.93 |
| $Pt/La_2O_3$ | 15.4 | 13.5 | 0.88 |
| $Pt/La_2O_3$–$ZrO_2$ | 15.5 | 24.2 | 1.56 |

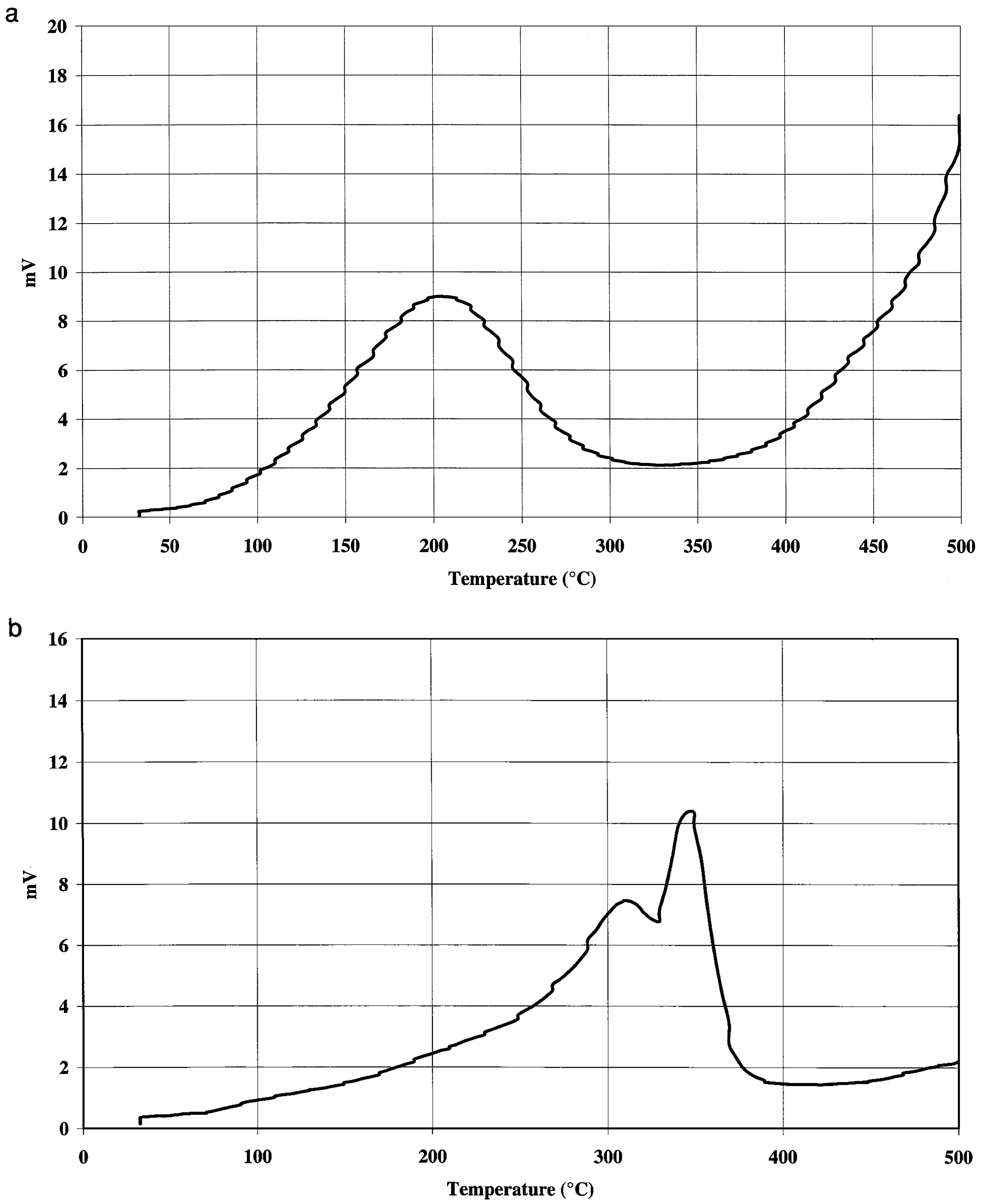

**FIG. 2.** TPR profile on (a) 1% Pt/$ZrO_2$, (b) 1% Pt/$La_2O_3$, and (c) 1% Pt/$ZrO_2$–$La_2O_3$.

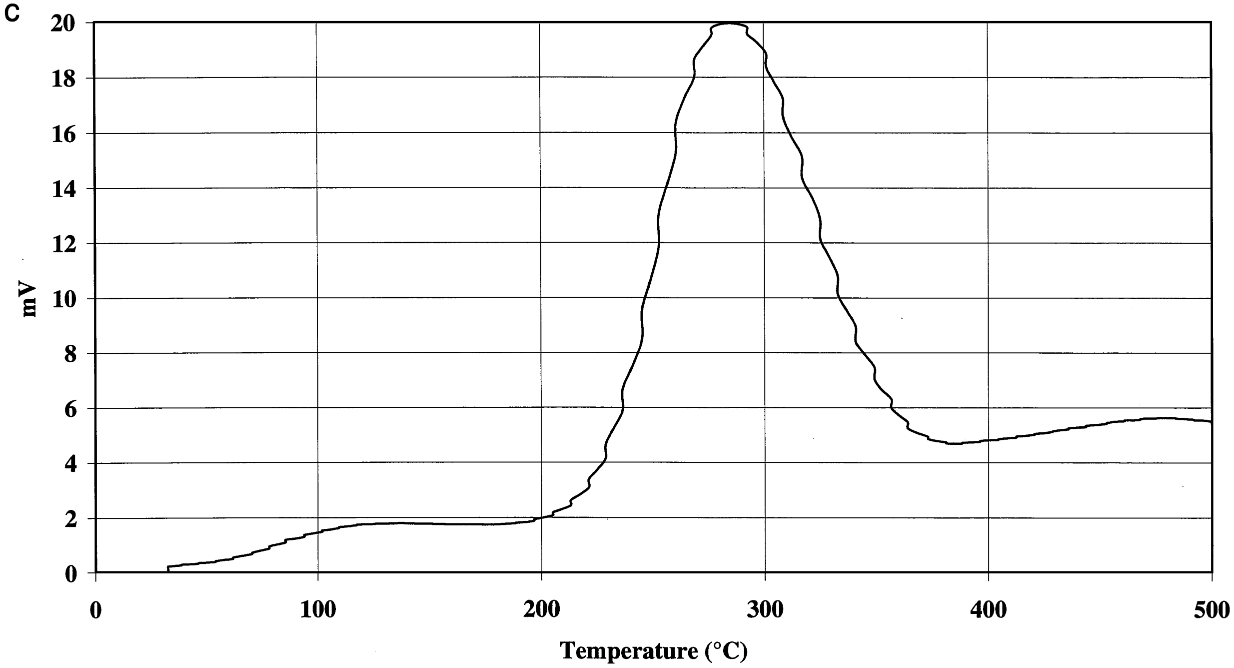

**FIG. 2**—*Continued*

experiments and due to the poor dispersion of the metal upon the surface, it is probable that the size distribution is heterogeneous and therefore the first peak is attributed to the reduction of large particles whereas the second peak represents the reduction of smaller particles generally more difficult to reduce (13). The case of $Pt/ZrO_2–La_2O_3$ is somehow different since the hydrogen consumed largely exceeds the amount required for the reduction of $PtO_2$. We do not have a clear explanation for this phenomenon, but it is possible that in this case a fraction of the support is reduced at the same time as the metal.

The difference in structure of the oxide observed either by XPS or TPR—PtO in one case and $PtO_2$ in the other—is due to the obligatory pretreatment prior to carrying out a TPR analysis. Indeed, an oxidising treatment under pure oxygen at 300°C for 4 h was applied in order to remove physisorbed water or other impurities. Therefore, it is very likely that the oxide structure was modified by such a treatment.

## 3.2. Catalytic Activity

### *3.2.1. Evaluation of Performance under Standard Mixture Conditions*

The conversions of NO and HC into $N_2$, $NO_2$, and $N_2O$ are shown in Figs. 3a, 3b, and 3c for $Pt/ZrO_2$, $Pt/La_2O_3$, and for $Pt/La_2O_3–ZrO_2$, respectively (CO and $CO_2$ are not displayed). In all cases, the conversion of NO increases to a maximum with the temperature before falling to zero above ca. 400°C. The maximum conversion for $Pt/La_2O_3$ and for $Pt/La_2O_3–ZrO_2$ is ca. 70% at 200°C, while $Pt/ZrO_2$ proves less efficient with a maximum of 50% at 250°C. The major product is $N_2$ which follows the NO curve with a maximum of ca. 50–55% for $Pt/La_2O_3$ and for $Pt/La_2O_3–ZrO_2$ while it is only 40% for $Pt/ZrO_2$. A point of differentiation between $Pt/La_2O_3$ and $Pt/La_2O_3–ZrO_2$ is the higher selectivity toward nitrogen formation on the part of the latter over a larger range of temperatures and as a consequence, a lower production of $NO_2$. For example, at 300°C, the overall NO conversion is equal to 56% for both catalysts; on $Pt/La_2O_3$, 18% of $NO_2$ is produced whereas only 11% is produced on $Pt/La_2O_3–ZrO_2$, which accounts for the difference in selectivity toward $N_2$ formation. Another difference, which should be pointed out, is the behaviour of the hydrocarbon whose combustion begins at a low temperature, as with NO, and is completed at ca. 400°C on $Pt/La_2O_3$– and $Pt/ZrO_2$ while a temperature of only 350°C is required to attain a full conversion by $Pt/La_2O_3–ZrO_2$.

As this catalyst exhibited quite a high activity for the conversion of both NO into nitrogen and the burning of HC under standard conditions, a series of experiments was designed and undertaken in an attempt to elucidate and understand the mechanism. Their description can be found in the sections following.

### *3.2.2. Mechanistic Studies*

*Nature of the reacting nitrogen oxide.* The nature of the nitrogen oxide active for SCR is the cause of some controversy in the literature. For example, Burch *et al.* consider that NO is adsorbed on reduced platinum (3), while Tanaka *et al.* propose a mechanism in which the oxidation of NO

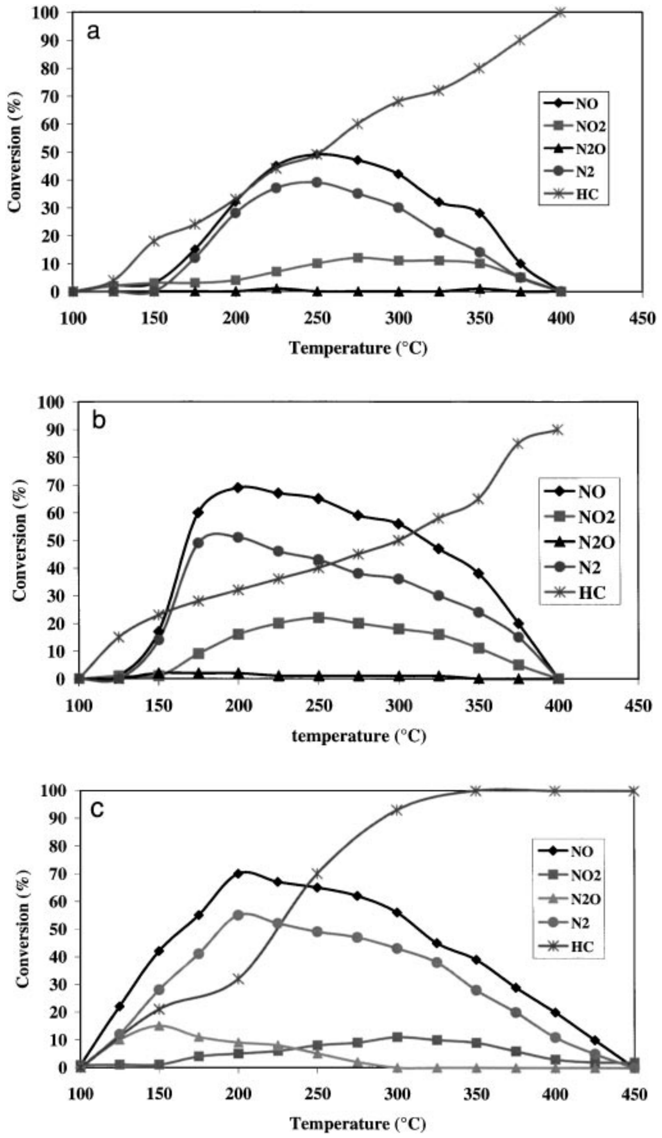

**FIG. 3.** Conversion of NO on (a) 1% Pt/$ZrO_2$ (500 ppm NO, 330 ppm HC, 350 ppm CO, 6% $O_2$, 12% $H_2O$, 10% $CO_2$), (b) 1% Pt/$La_2O_3$ (500 ppm NO, 330 ppm HC, 350 ppm CO, 6% $O_2$, 12% $H_2O$, 10% $CO_2$), and (c) 1% Pt/$La_2O_3$–$ZrO_2$ (500 ppm NO, 330 ppm HC, 350 ppm CO, 6% $O_2$, 12% $H_2O$, 10% $CO_2$).

into $NO_2$ is the first step (5). The activity for SCR was measured using $NO_2$ instead of NO as described when using standard conditions. Figures 4 and 5 show the evolution of the concentration of $NO_2$ with temperature in both the absence and presence of oxygen, respectively.

In the absence of oxygen, from 100°C, $NO_2$ is reduced to NO, this reaction being completed by 175°C. At this temperature, the concentration of NO is 500 ppm. Above 200°C, their concentration decreases because selective reduction by HC begins. There is also a small production of $NO_2$ and $N_2O$ beginning at 250°C (not represented in Fig. 4) which did not exceed 50 ppm. This experimental evidence proves that $NO_2$ is fully reduced to NO by decomposition upon the surface and that nitrogen is therefore produced by the reaction of NO with the hydrocarbon. In the absence of oxygen, NO is the molecule active for SCR.

In the presence of 6% oxygen, initially, $NO_2$ is entirely reduced into NO which then becomes the substrate for reaction with HC leading to nitrogen formation as the principal product. On the basis of this evidence, it appears clear that NO and not $NO_2$ is the reactive species.

### *3.2.3. Effect of Each Exhaust Gas Component upon Catalytic Activity*

This section of the work was undertaken in order to determine the influence of each individual reactant upon the overall reaction. The concentrations of oxygen, HC, and finally NO were studied by maintaining the concentrations of two of these constant while effecting a variation of the third.

*(i) Oxygen.* The reaction mixture contained 500 ppm of NO, 220 ppm $C_3H_8$, 110 ppm $C_3H_6$ while the $O_2$ concentration was varied between 0 and 10%. The results are presented in Fig. 6.

In the absence of oxygen, NO was converted between 200 and 300°C, the latter being the temperature at which the conversion reaches 100%. It is obvious by comparing Fig. 4 with Fig. 6, that NO is more reactive when issuing from $NO_2$ than from the gas phase when comparing the curve in the absence of oxygen. This implies that when $NO_2$ dissociates onto the surface, the NO formed and already adsorbed is more active than the one coming from the gas phase which has to overcome the barrier of energy needed to be adsorbed. In the presence of oxygen, reaction began at a lower temperature and the conversion followed a curve profile with a maximum at ca. 200°C. The conversion increased in parallel with the concentration of oxygen. This increase is not due to the formation of $NO_2$ but was the result of the formation of nitrogen. Both the dependence upon the oxygen concentration and the shape of the conversion curve invoke the hypothesis suggested previously about catalysts such as Cu-ZSM$_5$ with a reactive intermediate formed by a partial oxidation of the hydrocarbon adsorbed onto the surface as proposed by certain other authors (14–16). This intermediate should react directly with NO:

$$C_3H_6\text{-S} + 1/2\ O_2 \rightarrow C_3OH_6\text{-S}$$

$$C_3OH_6\text{-S} + 8\,NO\text{-S} \rightarrow 4\,N_2 + 3\,CO_2 + 3\,H_2O$$

The exact structure of the oxygenated intermediate is not described in the literature. Nevertheless, compounds such as aldehydes, alcohols, ketones, or carboxylates have been proposed.

*(ii) Hydrocarbon.* The reacting mixture contained 500 ppm of NO, 6% $O_2$ while the HC concentration was

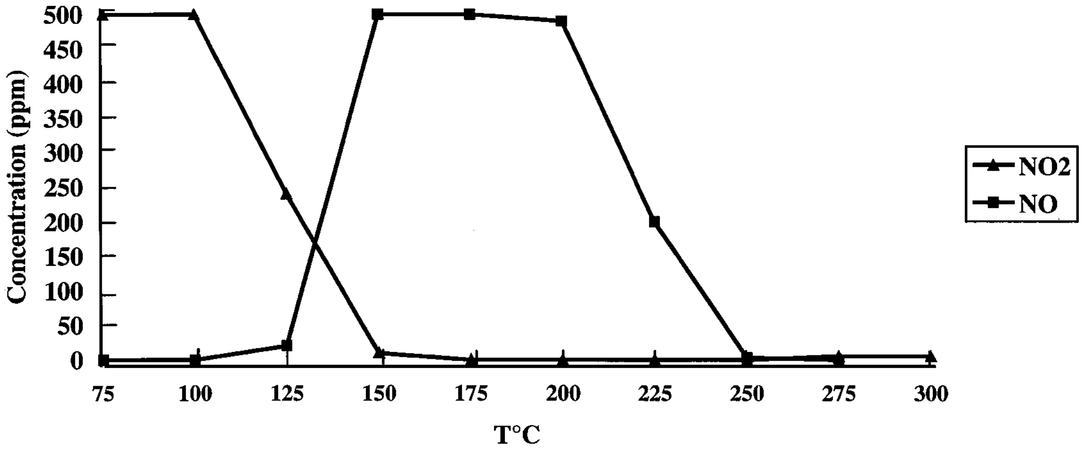

**FIG. 4.** Conversion of $NO_2$ on 1% $Pt/La_2O_3$–$ZrO_2$ in the absence of oxygen (500 ppm $NO_2$, 330 ppm HC).

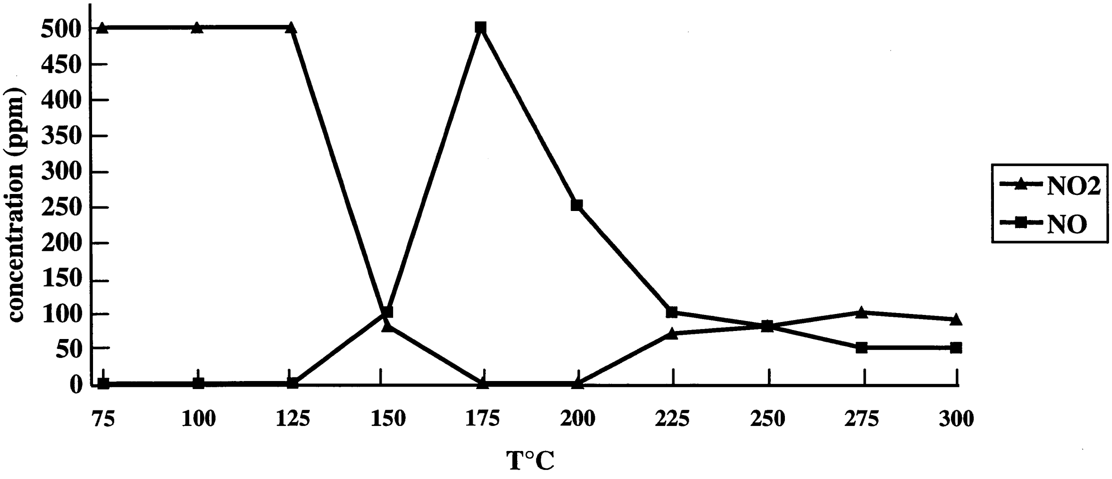

**FIG. 5.** Conversion of $NO_2$ on 1% $Pt/La_2O_3$–$ZrO_2$ in the precence of oxygen (500 ppm, $NO_2$, 330 ppm HC, 6% $O_2$).

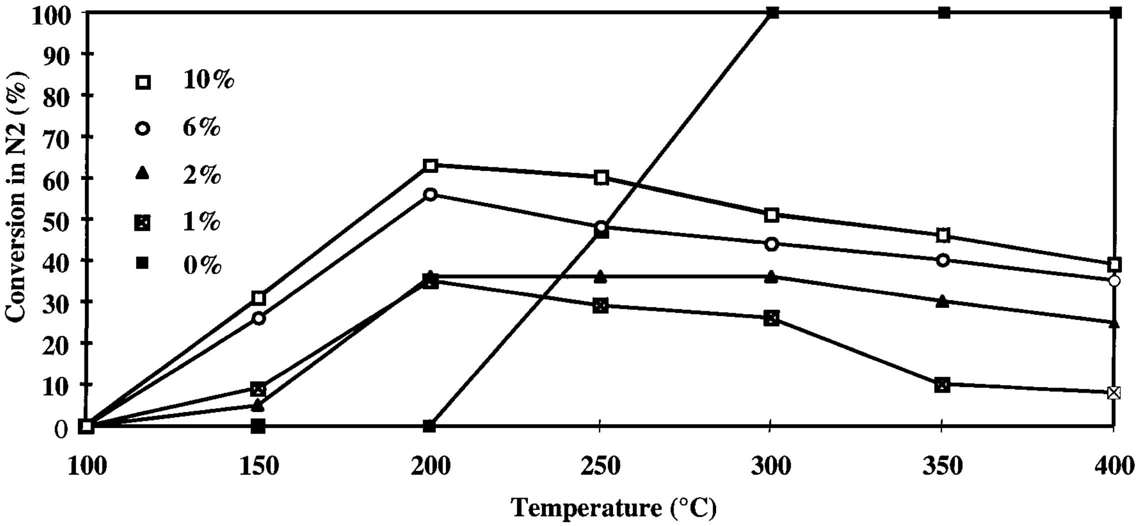

**FIG. 6.** Conversion into $N_2$ on 1% $Pt/La_2O_3$–$ZrO_2$ with a variation in the $O_2$ concentration (Composition: 500 ppm NO, 330 ppm HC and $O_2$).

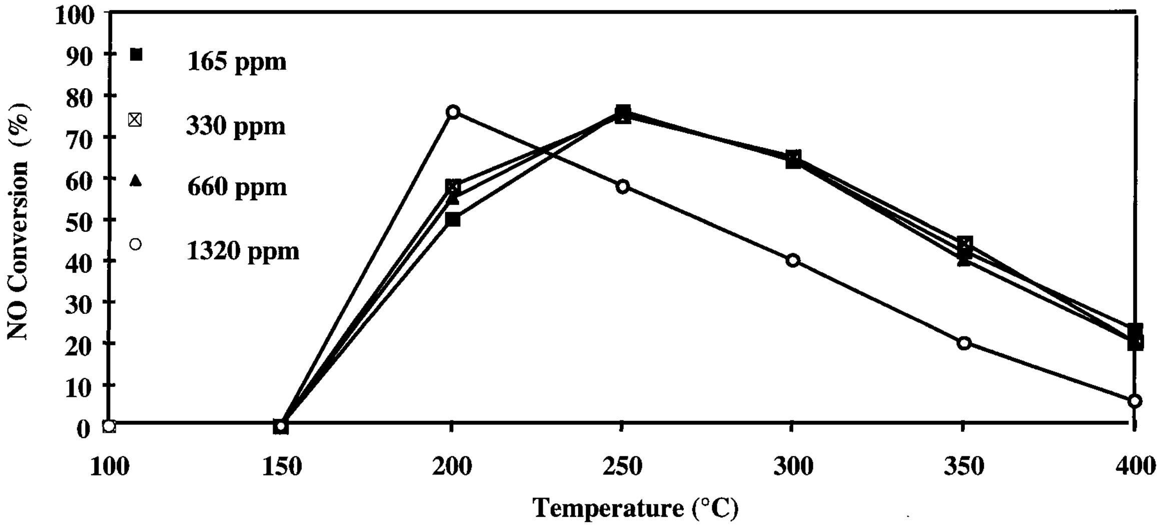

**FIG. 7.** NO conversion on 1% Pt/$La_2O_3$–$ZrO_2$ with variation in the HC concentration (Composition: 500 ppm NO, 6% $O_2$ and HC).

varied between 165 and 1320 ppm at a constant propane/propene ratio of 2. The results are presented in Fig. 7.

The conversion of NO appeared independent of the HC concentration between 165 and 660 ppm and reached ca. 75%. With 1320 ppm, the conversion proved more efficient below 220°C than above this temperature. The reactions between $C_3H_6$ or $C_3H_8$ and NO, respectively, could be written as:

$$9\,NO + C_3H_6 \rightarrow 4.5\,N_2 + 3\,CO_2 + 3\,H_2O$$

$$10\,NO + C_3H_8 \rightarrow 5\,N_2 + 3\,CO_2 + 4\,H_2O$$

Therefore, to reduce 500 ppm NO, only 50 ppm of $C_3H_8$ are required. The working conditions employed a large excess of HC when compared with the stoichiometric ratio. In the domain 165–660 ppm, the coverage is by HC. From a certain concentration, 1320 ppm in this case, there is an inhibition of the nitrogen production which could be the result of a competition for the adsorption site between NO and HC. Nevertheless, another possibility could be that from this concentration in HC, the reaction between HC and $O_2$ becomes predominant and therefore inhibits the reaction between HC and NO.

*(iii) NO.* The reaction mixture contained 330 ppm of HC, 6% $O_2$ while the NO concentration was varied between 250 and 1000 ppm. The results are presented in Fig. 8.

The conversion of NO increased with its concentration over the entire temperature range studied suggesting a

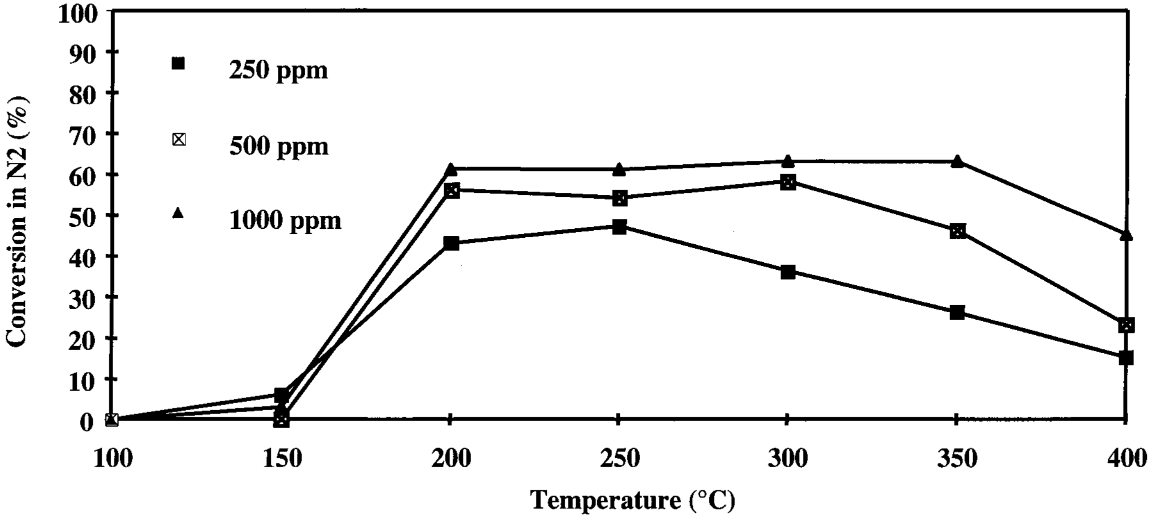

**FIG. 8.** Conversion into $N_2$ on 1% Pt/$La_2O_3$–$ZrO_2$ with variation of the NO concentration (Composition: 330 ppm HC, 6% $O_2$ and NO).

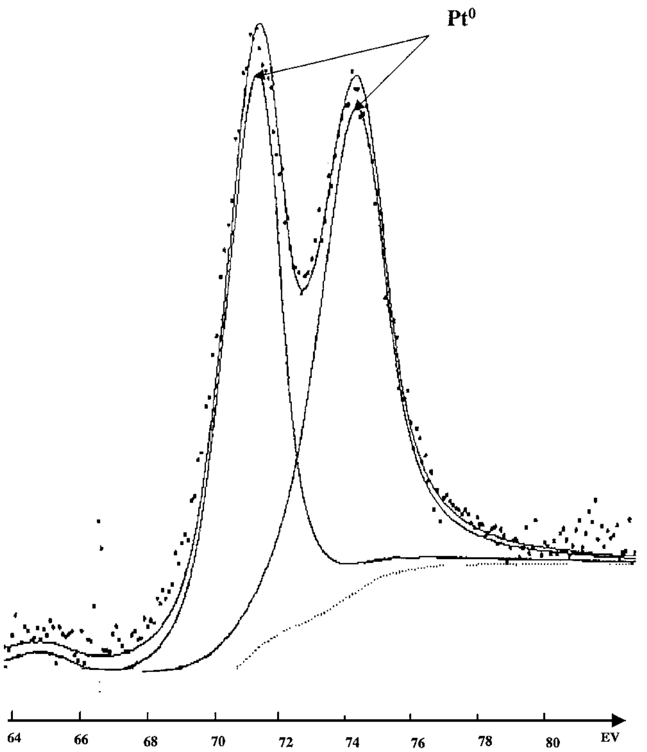

**FIG. 9.** XPS spectrum of 1% $Pt/La_2O_3–ZrO_2$ pretreated by pure hydrogen.

competitive adsorption between NO and HC. At 200°C, in the presence of 1000 ppm of NO the conversion to nitrogen was equal to ca. 60% which decreased to ca. 40% when 250 ppm of NO was used.

### 3.3. The State of the Metal During the Reaction

In Section 3.1, it was suggested that the platinum was in an oxidised state following the pretreatment. The mechanisms described in the literature suggest that the initial step of the reduction of NO consists of the decomposition of one molecule of adsorbed NO on a reduced platinum atom followed by its dissociation into N and O atoms and the subsequent recombination of 2 N atoms leading to molecular nitrogen. Although it is unlikely that the oxide could be reduced under the gas stream because it contains 6% $O_2$, this point was verified. Two methods were employed to evaluate the oxidation state of the metal. The first one comprised the use of the decomposition of NO as a probe reaction since it is known that such a reaction only occurs on reduced platinum (17, 18). The second method was by using XPS. In both cases, the results were compared with those obtained following a reducing pretreatment under pure hydrogen for 2 h at 400°C. The XPS spectrum of 1% $Pt/La_2O_3–ZrO_2$ shown in Fig. 9 proves that after such a treatment, only Pt° exists.

*(i) Reduction by Hydrogen*

The catalyst was heated twice successively from room temperature to 400°C under 500 ppm NO diluted in nitrogen. During the first reaction, the decomposition of NO into nitrogen and oxygen and $N_2O$ is possible from 200°C with a maximum of activity at 250°C as described by Fig. 10. Upon the second exposure to NO, the catalyst remained completely inactive. Following these two reactions, the catalyst was transferred to the XPS spectrometer. The spectrum on

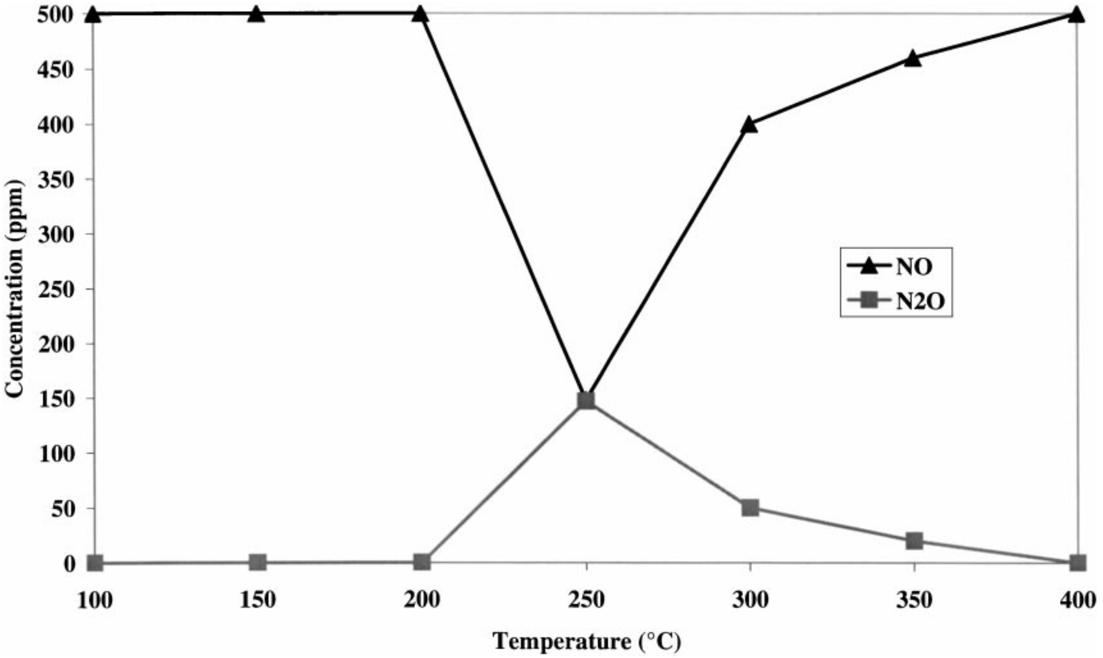

**FIG. 10.** NO decomposition on 1% $La_2O_3–ZrO_2$ pretreated by pure hydrogen.

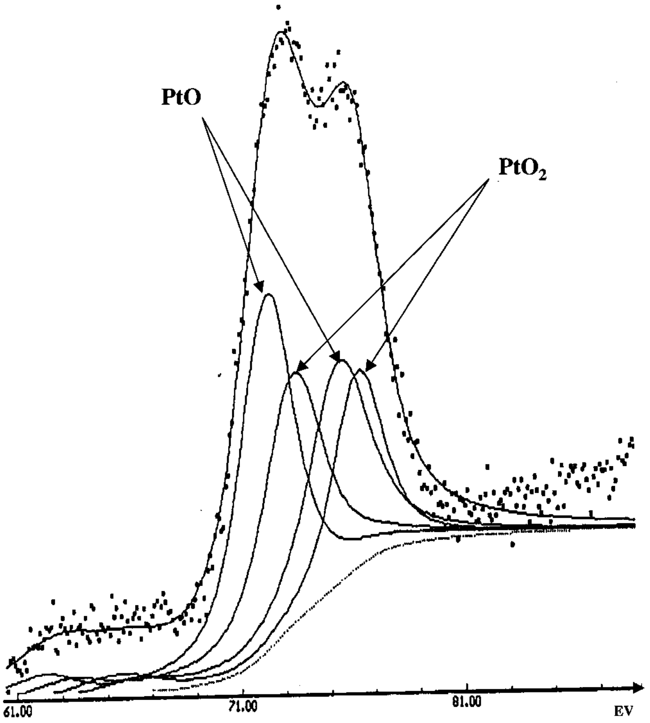

**FIG. 11.** XPS spectrum of 1% Pt/$La_2O_3$–$ZrO_2$ after two reactions at 550°C.

Fig. 11 reveals that the platinum is oxidised and composed of a mixture of PtO and $PtO_2$. The oxygen formed during the first reaction oxidises the metal into oxides inactive for the second reaction. Therefore, NO is dissociated exclusively upon reduced platinum. For the evaluation of the oxidation states of the metal this probe is most appropriate.

### *(ii) Reduction by the Hydrocarbons*

Since the only reducing agent in the reacting media was HC, the catalyst was submitted to an HC flow with a concentration equivalent to those used during the reaction (330 ppm) for 2 h in the pretreatment chamber of the spectrometer (Fig. 12). The figures reveal that during the reaction the platinum remained in the form of the oxides PtO and $PtO_2$. The reactants were unable to reduce it. If a stream containing 500 ppm NO is passed through this catalyst from room temperature to 400°C, again, no decomposition of NO is observed. This confirms that the platinum remains oxidised during the course of the reaction. Therefore, it is more than probable that the selective reduction of NO by HC will occur over platinum oxide and that reduced platinum is not an influencing factor.

## 4. DISCUSSION

Recently, several principal mechanisms for the selective reduction of NO$_x$ have been proposed in the literature. The mechanism, proposed by Burch *et al.* (3) is based upon the assumption that NO is dissociated upon metallic platinum issuing from its reduction by the hydrocarbon when using propene or an oxidised surface of platinum when using propane (19). The postulation that when using propene the surface coverage is dominated by carbonaceous species is reminiscent of the early mechanism proposed upon zeolites Cu-ZSM$_5$ where such deposits were involved as reaction intermediates (14). In various other proposals, the oxidation of NO into $NO_2$ occurs prior to reduction by HC (5, 20, 21). Also, possible intermediates such as an "oxy-hydrocarbon" (16, 22) or isocyanates, stable up to 300°C and observed by FTIR (6, 23), or by transient labelling techniques (24), have been reported.

Our results bring new elements to the continuing debate about the mechanism of SCR. In a first approach, the mechanism which involves the oxidation of NO into $NO_2$ as an initial step is unlikely since if $NO_2$ is introduced instead of NO as a reactant, the first step observed in our experimental conditions is its reduction into NO and then the profile of the reaction is similar to the one observed when using NO. Therefore, NO, and not $NO_2$ is the reacting species.

Our experiments have clearly shown that the dissociation of NO on reduced platinum sites does not exist under SCR conditions when using Pt/$La_2O_3$–$ZrO_2$. In this case, the metal remains fully oxidised during the course of the reaction since the HC was unable to reduce it and the SCR proceeds without NO dissociation occurring.

The literature remains unclear when the structure of an oxy-hydrocarbon is postulated as a reaction intermediate.

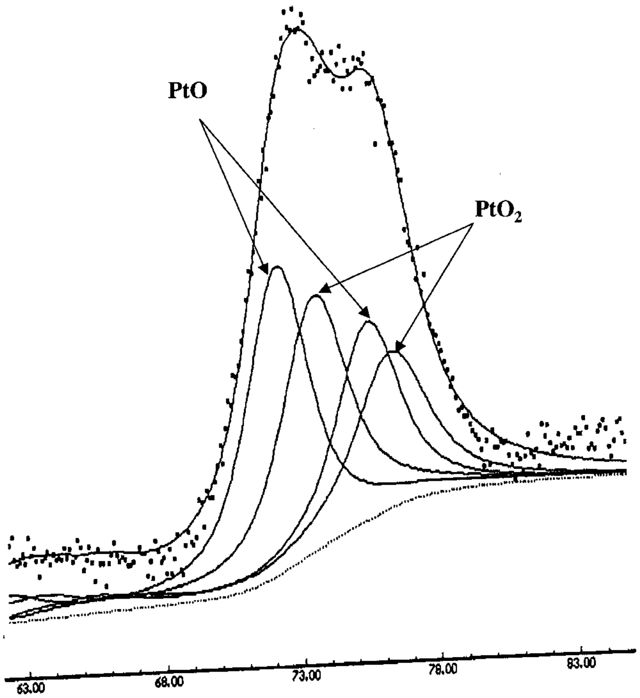

**FIG. 12.** XPS spectrum of 1% Pt/$La_2O_3$–$ZrO_2$ pretreated by 330 ppm of HC at 550°C.

It would seem that these species must possess at least a carbonyl group C=O. Our work has not yielded a definitive answer to this point. However, it is known that the transition metal oxides are good candidates for the reaction of hydrocarbon oxidation since they are able to adsorb them. Moreover, we have shown that the higher the oxygen concentration the greater the activity. Our opinion is that there is the formation of a bond between the hydrocarbon and an oxygen of the oxide.

Isocyanates have been implicated as reaction intermediates and were observed by FTIR following reduction under hydrogen. Our case is somehow different because of the oxidising nature of the surface. Nevertheless, some works report the existence of a bound $O_{support}$-N=O identified by FTIR on Cr oxide-type catalysts (nitrito species at 1140 and 1325 $cm^{-1}$). This would confirm the fact that it is possible for NO to be adsorbed without dissociation on an oxide.

In light of all these remarks, we propose a mechanism in which NO and HC compete for the same sites of platinum oxides. The adsorption of NO occurs via the surface oxygens and is favoured at high concentration reinforcing the idea of a rivalry between NO and HC. The HC is adsorbed on the platinum oxide sites where it is dehydrogenated by analogy with the reaction of hydrocarbon combustion. The breaking of a C–H bond is easier when Pt is oxidised (25). This interaction with a chimisorbed oxygen or a lattice oxygen allows the formation of an "oxy-type" intermediate which is then fully oxidised by either NO or oxygen depending upon the temperature. If the reactant is NO, then the probability of an intermediate existing which contains C, H, O, and N is increased. The study undertaken by Otto *et al.* gives interesting ideas on the species present on the surface (26). They show that the surface is predominantly covered by oxygen and that HC occupies less than 1% of the surface. The adsorption is favoured on large platinum particles and the authors propose a multisite adsorption of HC whose dissociation is favoured by the presence of excess oxygen.

The reactive species generated by the adsorbed HC could either reduce NO or be oxidised by oxygen. On our catalyst, the selectivity of NO reduction reaches its maximum around 200°C and decreases above this temperature where the HC reacts preferably with oxygen leading to a drop in the NO conversion and by consequence in the formation of nitrogen. The exact nature of the reaction intermediates we have not yet been able to establish. Nevertheless, some element of the answer can be found in the literature since Tanaka *et al.* (5), using FTIR, have pointed out the existence of nitro, nitrite, and carbonyl on $Pt/SiO_2$ and Bamwenda *et al.* (6) underline the importance of isocyanate compounds during the SCR on $Rh/Al_2O_3$.

## CONCLUSION

A careful study of the different factors influencing the catalytic reduction of $NO_x$ on platinum-based catalysts has been undertaken. The results obtained appear not to match exactly with the possible mechanisms proposed in the literature. The main findings are:

—NO, and not $NO_2$, is the molecule active for the reaction

—In the presence of oxygen, there is no carbonaceous deposits on the catalyst's surface.

A systematic study of the influence of the concentrations of the reactants (NO, HC, and $O_2$) indicates that there is a competition between NO and HC for the adsorption sites at temperatures where the conversion of NO is high. Although unable as yet to offer experimental evidence in support, we believe that the reaction intermediate is of the type $CtH_xO_yN_z$ and could correspond to an isocyanate, as already alluded to by several authors in the literature.

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