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A Transient Kinetic Study of the Mechanism of the NO/C_3H_6/O_2 Reaction over Pt–SiO_2 Catalysts

Part I: Non-Steady-State Transient Switching Experiments

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The mechanism of the reduction of NO by C_3H_6 under lean-burn conditions on a Pt catalyst has been investigated using transient techniques. Switches of O_2 and C_3H_6 into and out of a stream of C_3H_6/NO/O_2 over a 1% Pt–SiO_2 catalyst were performed at temperatures above and below that at which maximum NO_x conversion is seen, i.e., 220 and 250°C. The transient reaction studies show that at low temperatures the Pt is reduced and covered with carbonaceous material while at high temperatures it is oxidised and covered with O_{ads} species. Rapid changes in the surface oxidation state of the Pt are observed after the removal or reintroduction of the O_2 and C_3H_6 reactants at all temperatures. The results of each individual switch are discussed in terms of a mechanism for NO_x reduction and alkene oxidation over Pt-based catalysts in the "lean-NO_x" process. The conclusions are found to be consistent with our previous model for the NO_x reduction model. It is proposed that at low temperatures the NO reacts by decomposition on reduced Pt sites, whereas at high temperatures it reacts with O_{ads} on oxidised Pt to form NO_2. © 1999 Academic Press

Key Words: **Pt catalysts; lean-burn conditions; NO_x reduction; reaction mechanisms; transient kinetics.**

INTRODUCTION

The catalytic reduction of NO_x, using hydrocarbon reductants, in the presence of excess O_2 has been extensively studied over the past decade (1–11). It is now accepted that the prototype catalysts, Cu exchanged ZSM-5 zeolites, are not sufficiently stable to be of practical use in automotive exhaust catalysis (6). Supported Pt catalysts have also received much attention. These have good activities and selectivities at low temperatures but tend to form significant amounts of N_2O (7–18). There has been much debate in the literature (6–8, 10, 15) about the mechanism of NO reduction on Pt catalysts.

Detailed kinetic measurements in this laboratory support two different reaction mechanisms over these catalysts, the controlling mechanism depending of the type of hydrocarbon and the reaction temperature. It is proposed that when strongly reducing hydrocarbons, such as C_3H_6, are used at low temperatures the Pt is reduced and predominantly covered in carbonaceous species. The O_2 reacts to remove these carbonaceous species and the deNO_x reaction takes place through the dissociation of NO on vacant Pt sites (7). In the case of more weakly adsorbing reductants, such as C_3H_8, the reaction proceeds through an NO_2 intermediate (8). In this case the Pt surface is predominantly covered in adsorbed oxygen, NO is oxidised to NO_2 on the metal and moves to the support, or the metal–support interface, where it interacts with, and is reduced by, the impinging hydrocarbon molecules.

In the present work non-steady-state transient techniques have been used to attempt to obtain further confirmation of the previously proposed model by examining the Pt in the presence of C_3H_6, a strongly reducing hydrocarbon, both at low and high temperatures. A more detailed steady state isotopic transient kinetic analysis (SSITKA) will be presented in the companion paper (19).

EXPERIMENTAL

In order to be able to reduce effects caused by the interaction between the metal and the support, and discount reactions on the support itself, a Pt–SiO_2 catalyst is used throughout this study. The catalyst was prepared using incipient wetness impregnation of the required mass of a Pt(DNDA) solution (2.28% Pt) (DNDA = Di Nitro Di Amine) (Johnson Matthey) onto a pre-washed and dried sample of Grace SiO_2 with a grain size of 250–600 μm. The sample was dried at 110°C for 1 h and calcined in air at 500°C for 14 h. Surface areas and metal particle size measurements were performed on a homemade chemisorption apparatus. The sample of Pt–SiO_2 used had a total surface area of 280 $m^2\ g^{-1}$ and a metal dispersion of 22%.

Non-Steady-State Transient Reactions

In these experiments the sample (1% Pt–SiO_2) was pretreated for 1 h in the reactant stream at a temperature of

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480°C prior to the switches being carried out. These consisted of 2650 ppm NO, 2650 ppm C_3H_6 with 5% O_2 in the case of the O_2 switches and 2650 ppm NO, 1500 ppm C_3H_6 and 5% O_2 in the case of the C_3H_6 switches. A total flow of 200 cm^3 min^{-1} was used over a catalyst weighing 153 mg. The effluent gas was continuously monitored using a Gaslab 300 mass spectrometer coupled to the reactor using a heated evacuated capillary. Gas flows were blended into the He carrier from cylinders of NO, 1% C_3H_6 in He, O_2 and 5% Ar in He using mass flow controllers. The catalyst was held in a straight tubular quartz reactor between two plugs of glass wool in close contact with a thermocouple. The active phase was preceded by 100 mg of inert quartz chips which functioned both to preheat the gas flow and to guard against laminar flow through the catalyst bed.

Switches were carried out after the system had reached equilibrium at a particular temperature. These involved two gas lines flowing through a four-way valve, one exiting to blend with the reactant gas flow and moving on to the catalyst and the other exiting, through a fine needle valve, to vent. The pressure in the lines for the out-switched gas and the in-switched gas were equalised, i.e., the pressure in the in-switched line was raised to simulate the back pressure due to the catalyst, using two Wika pressure transducers and the needle valve. In this way either O_2 or C_3H_6 were switched out and a gas containing a 5% Ar tracer of the same pressure and flow switched into the reactant flow. Generally the reactant was switched out (and the inert tracer switched in) after 30 s and switched back in after 150 s with the experiment being stopped after 300 s. The data are presented as plots showing the normalised change in gas phase concentration before and after the switch. Therefore a value of 1 or 0 refers to the steady state concentration of this species on either side of the switch rather than to absolute gas phase concentrations.

Due to the lack of resolution of the mass spectrometer at the low gas pressures used it was not possible to monitor all the gas phase species during the same experiment and thus only two species were monitored during each switch, i.e., the inert tracer (Ar) and one other species. The results are then brought together at the end where the reproducibility of the argon trace was checked. In the cases where overlaps could be allowed for without overly affecting the resolution then these profiles were run together, e.g., m/e = 44 and m/e = 28.

RESULTS

Figure 1 shows a standard conversion versus temperature profile for the reduction of NO by C_3H_6 in the presence of an excess of O_2. It can be seen that maximum NO_x conversion is coincident with the point at which the hydrocarbon conversion first reaches ca. 100% and that NO_2 is only produced at temperatures above that at which the hydrocarbon is completely consumed. Under these reaction conditions the NO_x conversion peak occurs at ca. 230°C and thus gas switches were performed at temperatures below the peak (220°C) and above the peak (250°C), respectively. At temperatures above the peak the C_3H_6 is completely converted to CO_2 and there is a corresponding decrease in the gas phase O_2 concentration, while at temperatures below the peak, conversions of NO and C_3H_6 below 15% can easily be studied.

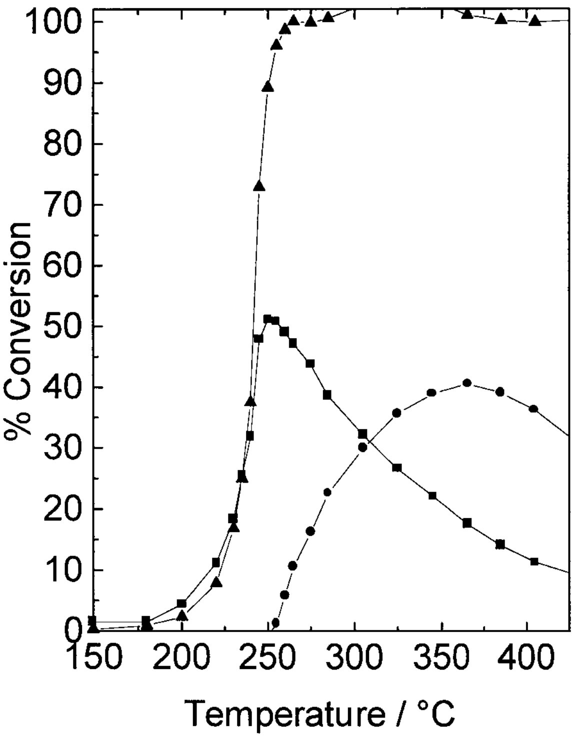

FIG. 1. The effect of temperature on the C_3H_6–NO–O_2 reaction over 1% Pt–SiO_2 Feed: 1000 ppm C_3H_6, 1000 ppm NO, 5% O_2 (▲ C_3H_6; ■ NO to N_2 and N_2O; ● NO to NO_2).

O_2 Switches at 220°C (Below the Temperature of Peak deNO$_x$ Activity)

Figure 2 shows the normalised responses observed at 220°C when O_2 is removed from the reaction stream and replaced with Ar. Under these conditions, according to the proposed mechanism of the reaction (7), the surface at steady state consists of mainly carbonaceous residues on reduced Pt sites with some vacant sites at which O_2 and NO can dissociate and react to form CO_2, N_2O, and N_2.

After the switch it is seen that the O_2 signal decreases exactly in line with the inverted Ar signal, i.e., the signal derived from the normalised Ar trace. A smoothed normalised C_3H_6 response is also shown. This is smoothed due to excessive noise (as only a minor change in C_3H_6 concentration is seen upon removing the O_2). To a first approximation it follows a short time behind the Ar curve as the O_2

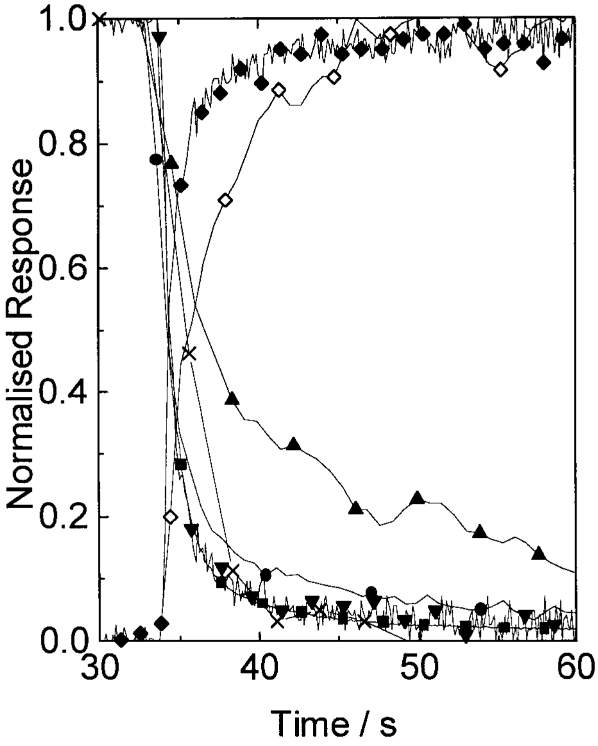

FIG. 2. Profiles obtained when O_2 was removed from the reactant stream over 1% Pt–SiO_2 and replaced with Ar. Feed: 2650 ppm NO, 2650 ppm C_3H_6, 5% O_2, $T = 220°C$ (■ O_2; ● CO_2–N_2O; ▲ CO–N_2; ◇ C_3H_6; × NO_2; ◆ Ar; ▼ Inv. Ar).

is switched out, indicating that very little time is needed for the surface to become saturated with C_3H_6-derived species. The CO_2 profile is also seen to be closely aligned with the Ar signal, indicating that there are only very small amounts of O_{ads} on the surface available to interact with the adsorbed carbonaceous species.

NO_2 production under these conditions is seen at very low levels. This ceases immediately when the O_2 is removed from the stream. Production of NO_2 would not be expected on the basis of the proposed mechanism of the reaction (7) but it must be remembered that under the present conditions the NO concentration is three times higher than has been used in the steady-state reaction measurements (Fig. 1). It is known that the homogeneous formation of NO_2 in the gas phase in the presence of an excess of O_2 is a reaction that depends on the concentration of NO to the second order.

The signal at m/e = 28 is seen to lag behind the Ar signal but it must be remembered that this might consist of CO as well as N_2. Due to the contributions to the m/e = 28 signal from both CO and CO_2 (as a fragment in the mass spectrometer) direct measurement of the N_2 change is not possible here. Even though CO is not produced over Pt catalysts under the steady-state conditions it is more likely to be formed under the hydrocarbon-rich conditions present after O_2 has been removed from the stream.

After 120 s, the O_2 is switched back in and the results are shown in Fig. 3. The O_2 trace is seen to rise with the inverted Ar signal while in this instance the CO_2 signal is seen to lag a significant time behind. The smoothed C_3H_6 signal also lags behind the Ar signal before returning to steady state. The NO_2 signal and the m/e = 28 signal also lag slightly behind the inverted Ar trace.

O_2 Switches at 250°C (Above the Temperature of Peak deNO$_x$ Activity)

The same experiments were then carried out at 250°C. Note that under these conditions the C_3H_6 conversion is 100% so it is not possible to obtain precise kinetic information. However, these experiments, and the corresponding switches of C_3H_6 from the reactant stream above light-off, which are discussed later, do show the generation of more homogeneous catalyst surfaces upon the removal of a reactant. Therefore some valuable information regarding the behaviour of the supported Pt catalysts under differing gas phase environments can be obtained.

It can again be seen (Fig. 4) that once O_2 is removed from the catalyst stream the O_2 and the N_2O/CO_2 signals follow the inverted Ar trace exactly while the C_3H_6 lags slightly behind the Ar trace. This lag in the behaviour of the C_3H_6 signal and the apparent carbon imbalance might be

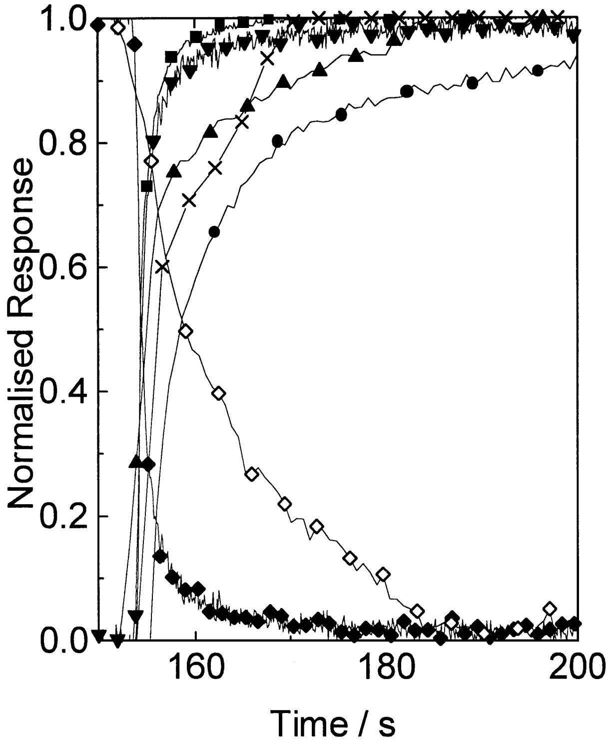

FIG. 3. Profiles obtained when O_2 was reintroduced to the reaction stream instead of Ar after 2 min in the O_2-free stream. Feed: 2650 ppm NO, 2650 ppm C_3H_6, 5% O_2, $T = 220°C$ (■ O_2; ● CO_2–N_2O; ▲ CO–N_2; ◇ C_3H_6; × NO_2; ◆ Ar; ▼ Inv. Ar).

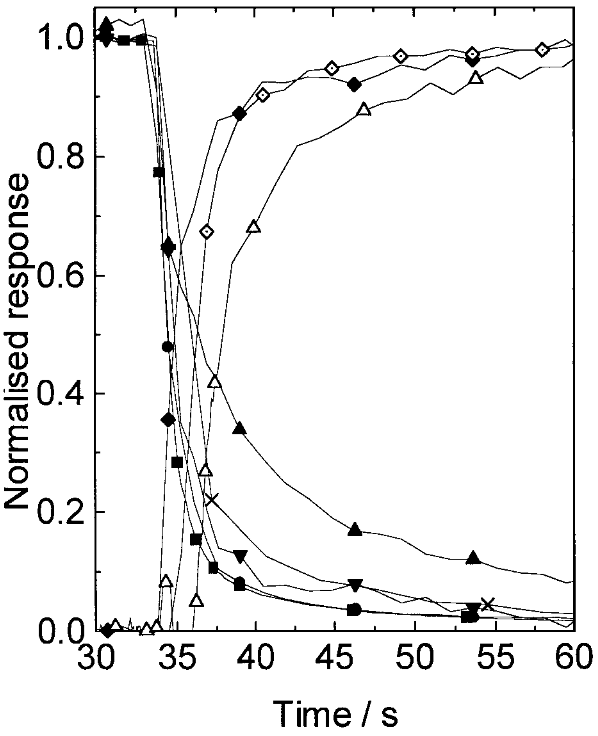

FIG. 4. Profiles obtained when O_2 was removed from the reactant stream over 1% Pt–SiO_2 and replaced with Ar. Feed: 2650 ppm NO, 2650 ppm C_3H_6, 5% O_2, $T = 250°C$ (■ O_2; ● $CO_2 + N_2O$; ▲ $CO + N_2$; △ NO; ◇ C_3H_6; × NO_2; ◆ Ar; ▼ Inv. Ar).

explained by the m/e = 28 signal which also shows a lag, as it decreases, after the O_2 is switched out. This again could relate to CO resulting from the reaction of the carbonaceous species with the decreasing amount of adsorbed oxygen atoms on the surface. The NO signal increases as the O_2 is switched out but is somewhat delayed and a pressure "spike" is seen as the switch is made.

The decrease in the NO_2 signal is also only slightly delayed relative to the inverted Ar, indicating that any O_{ads} species on the surface are not available for the production of NO_2 after a small period in the absence of O_2. The delay in the increase of the NO signal when O_2 is switched out shows that the surface is still capable of adsorbing and dissociating NO for a brief period in the absence of O_2.

When the O_2 is switched back in 120 s later (Fig. 5) the O_2 signal increases with the Ar, goes through a maximum, and returns to its steady-state level. The N_2O–CO_2 and C_3H_6 signals immediately begin to increase and decrease, respectively, albeit slightly delayed relative to the Ar. Both profiles go through inflexion points (the N_2O–CO_2 before the C_3H_6) before tending toward their steady-state values. The N_2O–CO_2 production increases to a level somewhat above the steady-state level before decreasing back to the steady state. Both profiles intersect at normalised values of 0.5 roughly 15 s after the switch.

When O_2 is switched back into the stream m/e = 28, i.e., N_2 and CO, production is seen to follow the CO_2 production, i.e., increasing immediately, going through an inflexion point, reaching a maximum, and then decreasing to the steady-state value. The NO signal also decreases immediately with the Ar signal until it reaches a value of 0.6 at which time the rate of decrease of the NO signal slows. The NO returns to a steady state value about 45 s after the switch.

Finally, the production of NO_2, an effective monitor of the surface state of Pt, is seen to increase rapidly after the CO_2 production has reached a steady state (ca. 20 s after the switch), indicating the presence of O atoms adsorbed on the Pt surface under these conditions.

C_3H_6 Switches at 220°C (Below the Temperature of Peak deNO$_x$ Activity)

When C_3H_6 is switched out of the reactant stream at 220°C (Fig. 6) a rapid increase is seen in the production of a peak at m/e = 44, which reaches a maximum after 2.1 s. This profile then decreases to its background level as the production of CO_2 decreases to zero in the absence of C_3H_6. Estimation of the amount of carbon deposited on the Pt surface under these conditions (as determined from the difference between the Ar profile and the m/e = 44 profile and taking the amount of CO_2 being formed at steady state) indicates

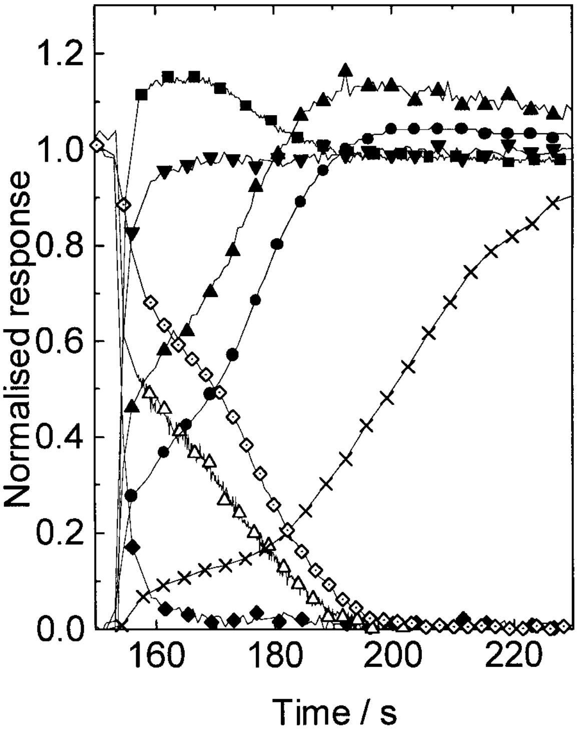

FIG. 5. Profiles obtained when O_2 was reintroduced to the reaction stream instead of Ar after 2 min in the O_2-free stream. Feed: 2650 ppm NO, 2650 ppm C_3H_6, 5% O_2, $T = 250°C$ (■ O_2; ● $CO_2 + N_2O$; ▲ $CO + N_2$; △ NO; ◇ C_3H_6; × NO_2; ◆ Ar; ▼ Inv. Ar).

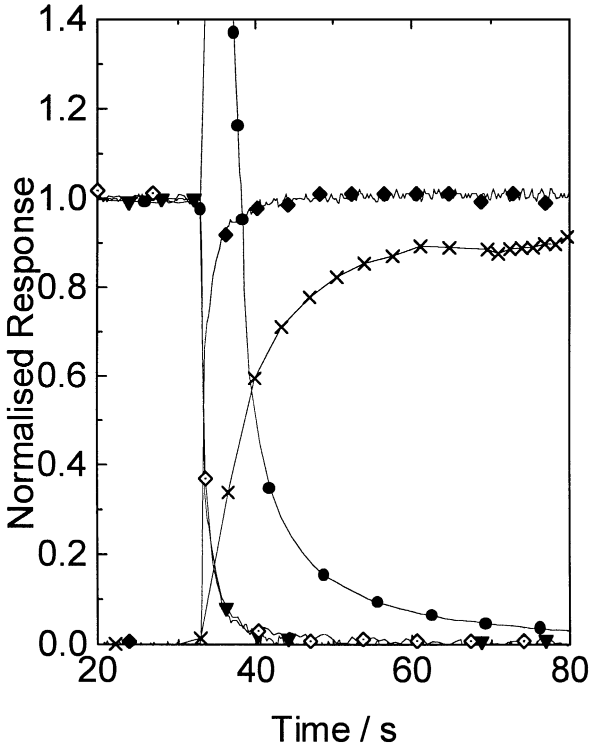

FIG. 6. Profiles obtained when C_3H_6 was removed from the reactant stream over 1% Pt–SiO_2 and replaced with Ar. Feed: 2650 ppm NO, 1500 ppm C_3H_6, 5% O_2, $T = 220°C$ (● $CO_2 + N_2O$; ◇ C_3H_6; × NO_2; ◆ Ar; ▼ Inv. Ar).

20 μmol of C_{ads} per gram of catalyst. This does not allow for the contribution of N_2O to this m/e signal and thus can only be taken as a rough estimate. This translates to almost two monolayers of C on the Pt surface under these conditions, i.e., $1.21 * 10^{19}$ atoms of C on a Pt surface of $6.79 * 10^{18}$ atoms.

NO_2 production is seen immediately and increases at a relatively slow rate to its steady-state value over ca. 43 s. The decrease in C_3H_6 concentration parallels exactly the decrease in the Ar signal, indicating that the adsorption of C_3H_6 onto the catalyst surface is irreversible.

When the C_3H_6 is switched back into the gas stream 120 s later, as seen in Fig. 7, the instantaneous production of m/e = 44 is seen. This profile peaks above the $CO_2 + N_2O$ steady-state values before decreasing back to the steady state after about 30 s. The C_3H_6 signal is delayed relative to the inverse Ar signal and reaches steady state at about the same time as the m/e = 44 signal. The NO_2 signal initially falls rapidly with the Ar but then returns slowly to its steady-state value.

C_3H_6 Switches at 250°C (Above the Temperature of Peak deNO$_x$ Activity)

The transitions from O_{ads}-covered to C_{ads}-covered Pt surfaces can be readily followed. The O_2 signal (Fig. 8) increases parallel to, but slightly behind, the Ar signal. The decrease in the CO_2 profile when the C_3H_6 is removed also lags somewhat behind the inverted Ar. This indicates that small amounts of carbonaceous species are on the surface at these temperatures.

The NO_2 profile increases gradually from its steady state reaction value as the surface is cleansed of remaining carbon and becomes oxygen saturated. The NO profile shows a gradually increasing trend and does not reach a normalised value until 100 s after the switch.

When the C_3H_6 is switched back into the stream 120 s later (Fig. 9) a profile due to C_3H_6 is seen which indicates that not all the hydrocarbon is oxidised immediately on the oxidised Pt surface. This is shown on a relative scale as the 0–1 normalised scale is meaningless in this case since the steady-state value of the C_3H_6 in the gas stream before and after the switch is zero. The presence of C_3H_6 in the gas phase is also slightly delayed, indicating that either the first molecules of gas to strike the surface were oxidised immediately or adsorbed. The O_2 profile decreases to its steady state value slightly behind the Ar. The CO_2 initially increases with the Ar, goes through an inflexion point and gradually rises, achieving steady state 22 s after the switch.

The NO_2 signal decreases rapidly with the Ar signal, goes through a minimum, and returns to the baseline 1 min after

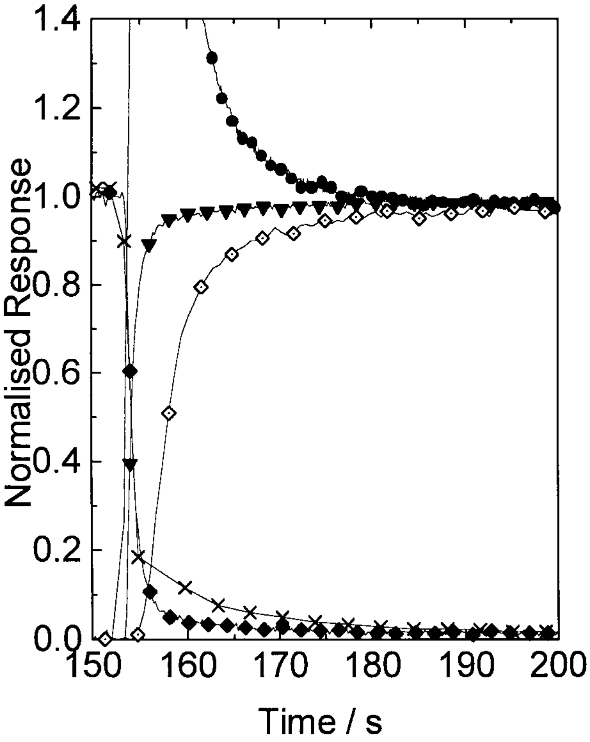

FIG. 7. Profiles obtained when C_3H_6 was reintroduced to the reaction stream instead of Ar after 2 min in the C_3H_6-free stream. Feed: 2650 ppm NO, 1500 ppm C_3H_6, 5% O_2, $T = 220°C$ (● $CO_2 + N_2O$; ◇ C_3H_6; × NO_2; ◆ Ar; ▼ Inv. Ar).

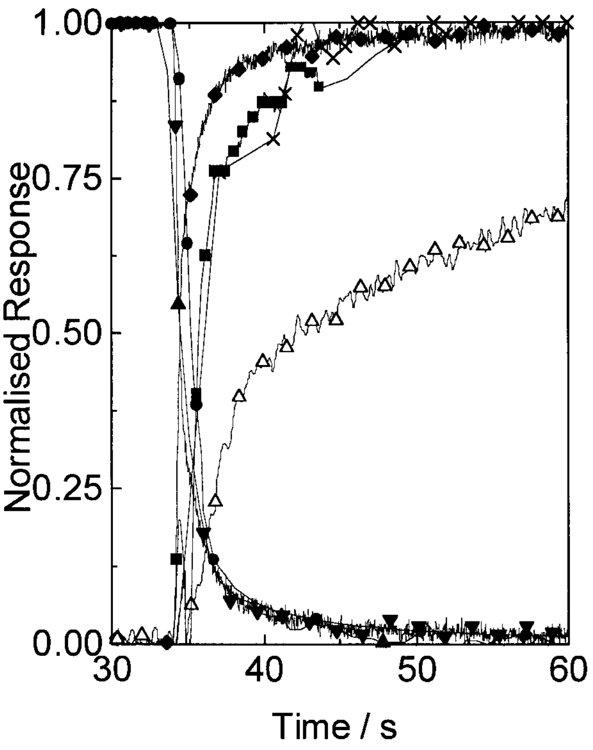

FIG. 8. Profiles obtained when C_3H_6 was removed from the reactant stream over 1% $Pt–SiO_2$ and replaced with Ar. Feed: 2650 ppm NO, 1500 ppm C_3H_6, 5% O_2, $T = 250°C$ (■ O_2; ● $CO_2–N_2O$; △ NO; ◇ C_3H_6; × NO_2; ◆ Ar; ▼ Inv. Ar).

the switch. It is interesting to note that the minimum seen in the profile for the NO_2 species coincides with the maximum seen in the transient response for the C_3H_6 signal. The NO signal also shows a sharp decrease immediately after the switch but then rises back to the normalised value of 1 before decreasing to the normalised value of zero over a period of 40 s. The reason for the original sharp decrease is probably due to the interference in the NO signal from the NO_2 signal.

DISCUSSION

The non-steady-state transient experiments described above can provide information about how the surface relaxes from its steady state, in which it produces N_2 and N_2O from NO, to one of two inactive states during which this does not take place. These are the fully oxidised $Pt–O_x$ state and the fully reduced C_xH_y-covered Pt state. As mentioned previously, switches above the temperature of the peak in NO_x reduction are not as valuable as those obtained below this critical temperature because of the high conversion of C_3H_6, but the results can still provide information on the delicate interplay between the amounts of oxygen and hydrocarbon adsorbed on the catalyst under reaction conditions.

The first important point to note from our results is that under reaction conditions O_2 and C_3H_6 are both adsorbed irreversibly onto the catalyst surface. If this was not the case then a chromatographic delay in the decrease in the concentration of C_3H_6 or O_2 relative to Ar would have been observed once they were interchanged in the reactant stream (in Figs. 2 and 6). Therefore, under our experimental conditions, oxygen and C_3H_6 are both strongly adsorbed on the surface of the Pt.

From the O_2 and C_3H_6 switches below the temperature of maximum NO_x conversion (220°C) we find evidence that at steady state the Pt is heavily covered with carbon. Removal of the O_2 rapidly results in the generation of a totally carbon-covered surface, whereas removal of the C_3H_6 only gradually results in the formation of a surface that is covered in O_{ads}. In contrast, the switches above the temperature of maximum NO_x conversion are consistent with a surface which is predominantly covered in O_{ads} species.

The level of NO_2 production provides a valuable indication of the surface state of the catalyst. When O_2 is removed from the catalyst at 220°C the NO_2 concentration drops exactly in line with the O_2 and the Ar. Reintroduction of the O_2 into the reactant stream rapidly results in the same small level of NO_2 being formed. Conversely, when C_3H_6 is removed from the reactant stream, the formation

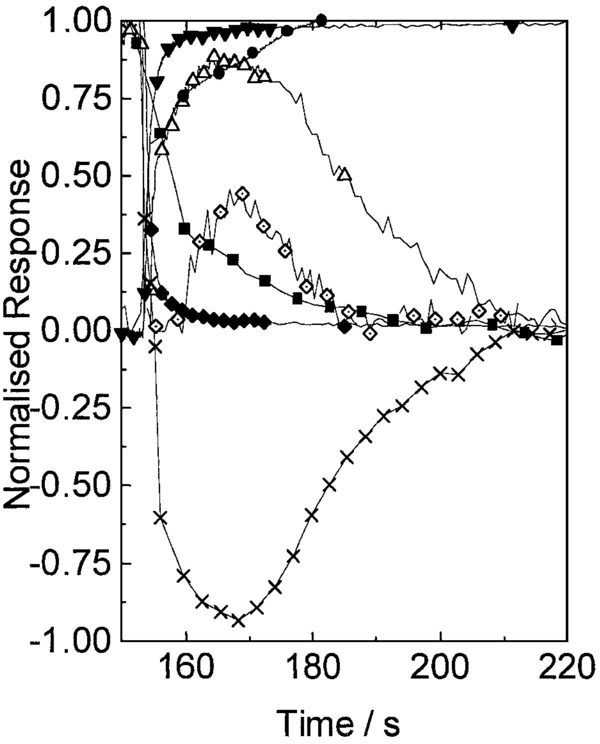

FIG. 9. Profiles obtained when C_3H_6 was reintroduced to the reaction stream instead of Ar after 2 min in the C_3H_6-free stream. Feed: 2650 ppm NO, 1500 ppm C_3H_6, 5% O_2, $T = 250°C$ (■ O_2; ● $CO_2–N_2O$; △ NO; ◇ C_3H_6; × NO_2; ◆ Ar; ▼ Inv. Ar).

of NO_2 is almost instantaneous (Fig. 6). This NO_2 is formed on the (oxidised) catalyst. The amount of NO_2 reaches a maximum when the m/e = 44 signal (CO_2) returns to the baseline. This is simply because at this point the surface is free of carbonaceous deposits and the concentration of O_{ads} has reached its maximum level and therefore the Pt has the maximum activity for the production of NO_2 via an $NO + O_{ads} \rightarrow NO_2$ reaction.

Another informative feature of the NO_2 profile can be seen in Fig. 9 (where C_3H_6 is reintroduced to the $NO + O_2$ stream). Here the NO_2 decreases from a steady-state level of 1, decreases to a level of ~ -0.9, and increases to the new steady-state level of 0. This indicates that the catalyst changes from a fully oxidised state ($NO_2 = 1$), via a less oxidised state ($NO_2 < 0$), to its steady-state level of oxidation ($NO_2 = 1$). The fact that the C_3H_6 level in the stream reaches a maximum when the NO_2 level reaches a minimum also supports this view of the state of the surface.

Information about the mechanism of oxidation of C_3H_6 on these catalysts under NO_x reduction conditions can also be determined. The m/e = 44 profile when C_3H_6 is switched off (see Fig. 6) shows that the rate of CO_2 formation is limited by the concentration of adsorbed O atoms on the catalyst surface. O_2 is not readily adsorbed in competition with C_3H_6 so under steady-state conditions the Pt surface is deficient in O_{ads} and the rate of C_3H_6 oxidation is low.

These results provide further evidence in support of our model (7) for the NO_x reduction reaction with C_3H_6, namely that under normal steady-state conditions the Pt is in a reduced, carbon-covered state. This is the case even though the reaction mixture contains a 50 : 1 molar excess of $O_{2(g)}$ with respect to $C_3H_{6(g)}$. Thus, in our experiments on the NO_x reduction by C_3H_6 at 220°C, there are several points we can make about the Pt surface both under steady-state conditions and in the two extreme cases of total oxidation and total reduction:

- the adsorption of O_2 and C_3H_6 is irreversible;
- the detection of NO_2 can be regarded as indicative of the presence of Pt-O species on the surface;
- the combustion reaction at steady state is limited by the O_{ads} concentration on the Pt surface;
- $C_3H_{6(g)}$ can interact directly with an O_{ads} covered surface to form CO_2 whereas the reverse reaction, $O_{2(g)}$ reacting directly with a C_{ads} covered surface, needs an induction time as O_2 has to adsorb and dissociate.

The experiments performed for catalysts held above the NO_x peak (250°C) also demonstrate these points. Figure 5 (where O_2 is switched over a C_{ads}-covered surface at 250°C) shows the induction time needed for O_2 to reach its steady state. The concentration actually rises above its steady-state value before decreasing to the normalised value roughly 40 s after the switch. This is due to the fact that the catalyst is carbon-covered and there is an induction time before the steady-state rate of O_2 adsorption and dissociation is established. Similarly, the NO_2 level changes from a value of zero shortly after the switch, as some O_{ads} populates the surface, but does not reach a value of unity until the hydrocarbon is fully consumed and the surface has a steady-state concentration of O_{ads}.

CONCLUSIONS

The surface states of supported Pt catalysts have been probed using a series of non-steady-state transient switching experiments. While these observations contain no direct evidence regarding the mechanism of the deNO_x reaction over the catalyst, important information regarding the surface species on the metal under the reaction conditions has been deduced from the profiles obtained.

The surface of SiO_2-supported Pt catalysts can be thought of as varying between two extremes during the $NO/C_3H_6/O_2$ reaction. First, the surface is predominantly carbon covered and reduced at low temperatures in a C_3H_6-containing atmosphere even though the gas mixture contains a very large excess of O_2. C_3H_6 is adsorbed strongly and irreversibly on the surface. The carbon-covered surface can be oxidised at these temperatures by removing the C_3H_6 from the gas phase. Conversely at higher temperatures the surface is predominantly oxidised. Removal of the O_2 from the reaction streams results in reduction and a build up of carbon on the surface while removal of C_3H_6 results in further oxidation of the surface relative to its steady state. Overall the results are consistent with the model for the reduction of NO by hydrocarbons under lean-burn conditions proposed previously (7, 8).

To summarise, at low temperatures Pt is reduced and active for NO decomposition while at high temperatures Pt is oxidised and converts NO to NO_2.

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