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Selective reduction of nitrogen oxides by hydrocarbons under lean-burn conditions using supported platinum group metal catalysts

R. Burch *, P.J. Millington

Catalysis Research Group, The University of Reading, Whiteknights, Reading RG6 2AD, UK

Abstract

The performance of supported platinum-group metals (Pt, Pd, Rh, Ir and Ru) for the selective reduction of nitrogen oxides by hydrocarbons under oxidising conditions is reviewed. Kinetic and mechanistic studies on these catalysts are assessed. Many of the factors influencing de-NO_x behavior are considered. These include the choice of metal, the metal loading and the metal particle size, the carbon number and hydrocarbon type of the reductant used and the type of support material. It is found that highest de-NO_x activity is obtained with platinum-based catalysts although large quantities of nitrous oxide are formed in addition to nitrogen. Rhodium also exhibits a significant but lower activity although much less N_2O is produced. It is seen that NO_x reduction is coincident with hydrocarbon combustion. Although metal particle size has little effect on overall de-NO_x activity, large particles have higher turnover frequencies. For a given carbon number, it is found that the de-NO_x efficiency increases in the order i-paraffins < aromatics < n-paraffins < olefins ≈ alcohols and that, in general, activity increases with increasing carbon number. When using olefins as the reductant, varying the support material has little effect on activity although large differences can be seen when using saturated hydrocarbons. Mechanistic studies, including FT-IR and TAP experiments, are reviewed and the various mechanisms that have been proposed for this reaction are discussed.

Keywords: NO_x; Reduction; Lean-burn catalysts; Platinum catalysts

1. Introduction

Much recent research on the selective reduction of nitrogen oxides by hydrocarbons under lean-burn conditions has been concerned with zeolite-based systems, in particular the ubiquitous Cu-ZSM5 catalysts. However, as has been pointed out very clearly elsewhere in this special issue of *Catalysis Today*, [1,2] there are major problems with these catalysts both in terms of their thermal stability, and in terms of their sensitivity to water. There is, therefore, an urgent need to identify catalysts which have the potential to be commercially viable. One possible type of catalyst is based on the platinum group metals since these are already used in conventional (stoichiometric) exhaust gas cleanup and have proven stabilities and tolerance to typical potential poisons in the engine exhaust. It will become apparent later in this review that simple systems based on the platinum group metals may not be adequate for the very demanding challenge of providing high activity, good selectivity, and a wide operating temperature range. For example, with platinum, which is one of the better catalysts, the formation of nitrous oxide (N_2O) is

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* Corresponding author.

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a major problem which is yet to be solved. Nevertheless, these catalysts do hold out some promise and so a better understanding of their characteristic properties, and the likely mechanism of the selective lean-burn reduction reaction could provide a valuable basis for the logical design of catalysts with enhanced properties.

Relatively few groups have as yet published work on these systems [3–9]. However, there is sufficient information available in the open literature to begin to see patterns of behaviour and to provide some insight into tentative reaction mechanisms. The aim of this review is to critically assess the experimental information currently available on supported platinum group metal catalysts under the headings of (a) kinetic results and (b) mechanistic studies. This information will then be used to derive a tentative reaction model in the hope that this may facilitate the design of improved catalysts. Although there has been some work on zeolite-based platinum group metal systems, this will not be discussed in detail here since it seems that with the possible exception of Pt, these systems are either inactive or have insufficient stability for practical application.

2. Kinetic results

A number of groups have investigated Pt, Pd and Rh catalysts, supported mainly on alumina or silica, using propane or propene as model hydrocarbon reductants. There have also been a few results published on Ir and Ru catalysts, and for Pt or Pd on other supports or with other reductants. Table 1 summarises the main results which have been published in the open literature in a form which makes comparison convenient or possible: some results using commercial catalysts with a wider range of reductants will be discussed later.

The results in Table 1 refer only to specific temperatures and it is important to recognise that the selective reduction of nitrogen oxides is very dependent on temperature, gas composition, choice of catalyst, etc. (see later). However, in broad terms the results summarised in Table 1 can be used to underline a number of important points.

With propene as a reductant Rh is moderately active for the formation of N_2 but this is only at the upper end of the temperature range (ca. 300°C). There is not much N_2O formed with Rh catalysts, which is consistent with the known properties of Rh under stoichiometric conditions. Alumina-supported Rh seems to be more active than Rh/SiO_2 but in the absence of information on particle size distributions it is not possible to ascribe this to any particular property of the two catalysts. In Hamada's work [5], the Rh/SiO_2 is less selective towards N_2 relative to N_2O than is the case with Rh/Al_2O_3. Ru seems to be quite selective at lower temperatures but a poor catalyst at higher temperatures. Pd is also not a very good catalyst irrespective of the choice of support.

Table 1 shows that Pt is the best catalyst under these experimental conditions, although it produces a lot of N_2O and, indeed, this is a serious deficiency in Pt catalysts for this reaction. Depending on the choice of catalyst and the operating conditions the proportion of NO converted to N_2O rather than N_2 varies from ca. 25–80%. Where it is possible to make comparisons there seems not to be much difference between Pt/Al_2O_3 and Pt/SiO_2 catalysts with propene as the reductant.

When the reductant is propane, none of the platinum group metals is very selective or active. Where there is a reasonable activity, normally at higher temperatures, a substantial amount of N_2O is observed. It is interesting that in the case of the Pt catalysts with propane the Pt/Al_2O_3 shows some (small) activity at higher temperatures, but Pt/SiO_2 appears to be completely inactive.

Engler et al. [7] have examined the catalytic reduction of nitrogen oxides in diesel exhaust gas using a Pt-based monolithic sample. They have used a variety of experimental conditions, including model gas compositions comprising CO, H_2 and hydrocarbons, as well as SO_2, CO_2, and H_2O. The hydrocarbons have varied from methane to hexadecane, ethene to oct-1-ene, methanol to 1-butanol, and toluene through various xylenes to 1-methylnaphthalene. These results are shown

Table 1
Activity and selectivity data for the selective reduction of NO on various supported platinum group metal catalysts

Catalyst [ref.]	NO (ppm)	HC (ppm)	O_2 (%)	SV[a]	C^b_{NO}	Reaction temperature (°C)		
						200	250	300
$Pt/B_2O_3/SiO_2/Al_2O_3$ [3]	1000	C_3H_6 (1000)	5	30–60	N_2	24.7	10.2	6.3
					N_2O	25.0	6.7	2.7
$Pt/AlPO_4$ [3]	1000	C_3H_6 (1000)	5	30–60	N_2	17.9	5.8	4.0
					N_2O	14.5	6.3	5.1
$Pt/AlPO_4$–SO_4 [3]	1000	C_3H_6 (1000)	5	30–60	N_2	32.2	21.9	3.9
					N_2O	4.8	3.3	0.5
Pt/Al_2O_3 [4]	995	C_3H_6 (870)	5	160	N_2	11.1	17.8	3.3
					N_2O	3.3	34.4	–
Pt/SiO_2 [5]	1000	C_3H_6 (918)	10	300	N_2	12.0	8.0	5.0
					N_2O	40.0	21.0	14.0
Pt/Al_2O_3 [5]	1000	C_3H_6 (918)	10	300	N_2	10.0	4.0	2.5
					N_2O	34.0	20.0	5.0
$Pd/B_2O_3/SiO_2/Al_2O_3$ [3]	1000	C_3H_6 (1000)	5	30–60	N_2	7.6	7.9	4.7
					N_2O	10.1	5.6	5.1
Pd/SiO_2 [5]	1000	C_3H_6 (918)	10	300	N_2	0.0	3.0	2.0
					N_2O	2.0	9.0	6.0
Pd/Al_2O_3 [5]	1000	C_3H_6 (918)	10	300	N_2	8.0	9.0	3.0
					N_2O	3.0	5.0	3.0
$Ir/B_2O_3/SiO_2/Al_2O_3$ [3]	1000	C_3H_6 (1000)	5	30–60	N_2	20.9	9.0	3.6
					N_2O	11.8	5.3	10.6
$Ru/B_2O_3/SiO_2/Al_2O_3$ [3]	1000	C_3H_6 (1000)	5	30–60	N_2	20.3	6.0	–
					N_2O	4.2	0.2	–
Rh/Al_2O_3 [4]	995	C_3H_6 (870)	5	160	N_2	4.4	8.9	42.2
					N_2O	0.0	2.2	4.4
Rh/SiO_2 [5]	1000	C_3H_6 (918)	10	300	N_2	0.0	3.0	9.0
					N_2O	0.0	4.0	11.0
Rh/Al_2O_3 [5]	1000	C_3H_6 (918)	10	300	N_2	3.0	22.0	22.0
					N_2O	1.0	5.0	9.0
Pt/Al_2O_3 [6]	1079	C_3H_8 (323)	10	62	N_2	–	–	10.0
Pt/Al_2O_3 [5]	1000	C_3H_8 (973)	10	300	N_2	1.0	–	14.0
					N_2O	3.0	–	12.0
Pt/SiO_2 [5]	1000	C_3H_8 (973)	10	300	N_2	0.0	0.0	0.0
					N_2O	0.0	0.0	0.0
Pd/Al_2O_3 [5]	1000	C_3H_8 (973)	10	300	N_2	0.0	3.0	12.0
					N_2O	0.0	2.0	12.0
Pd/SiO_2 [5]	1000	C_3H_8 (323)	10	300	N_2	–	–	2.0
					N_2O	–	–	1.0
Rh/SiO_2 [5]	1000	C_3H_8 (323)	10	300	N_2	–	–	1.0
					N_2O	–	–	1.0
Rh/Al_2O_3 [5]	1000	C_3H_8 (973)	10	300	N_2	2.0	6.0	19.0
					N_2O	0.0	1.0	7.0

[a] Gas flow-rate in $cm^3\ min^{-1}\ gcat^{-1}$.

[b] Percentage conversion of NO to N_2 or N_2O.

graphically in Fig. 1, Fig. 2, Fig. 3 and Fig. 4.

The main points from the work of Engler et al. are as follows: linear paraffinic hydrocarbons show (Fig. 1a and Fig. 1b) NO_x conversion only at higher carbon numbers ($n > 4$ in C_nH_{2n+2}). The increasing effectiveness with increasing carbon number becomes smaller as 'n' increases so that n-heptane and n-hexadecane seem to have iden-

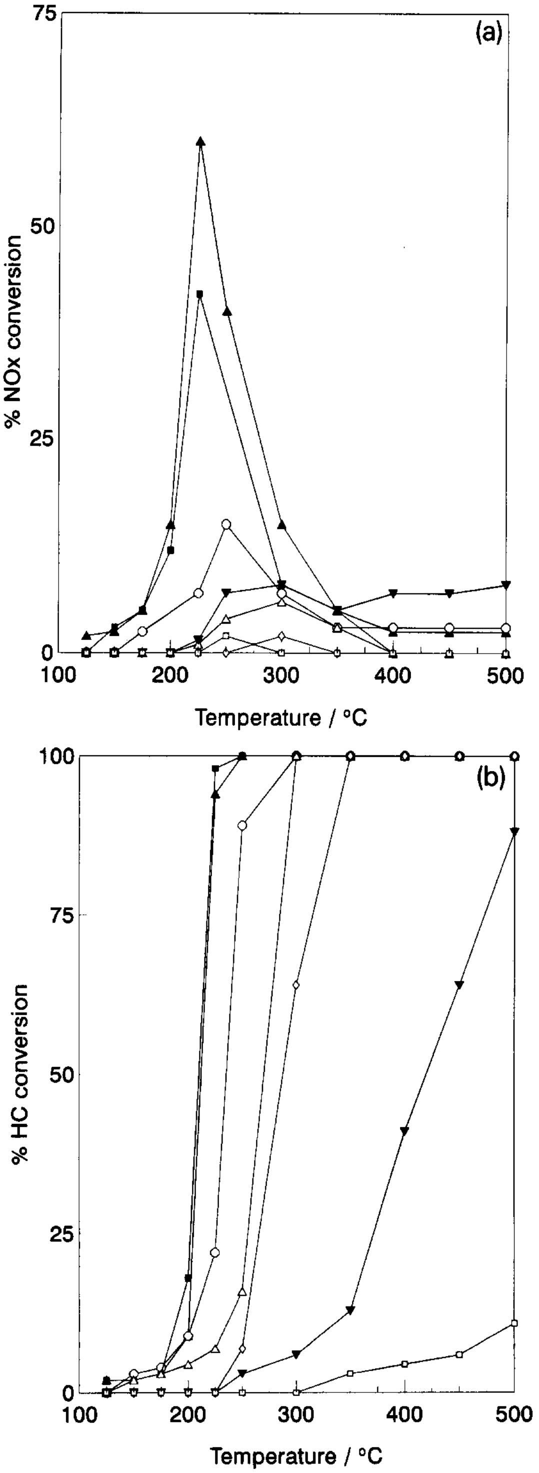

Fig. 1. (a) NO_x and (b) HC conversion as a function of temperature using paraffinic hydrocarbons on a Pt catalyst: (□) methane, (▼) ethane, (◇) propane, (△) n-butane, (■) n-heptane, (○) i-octane, (▲) n-hexadecane.

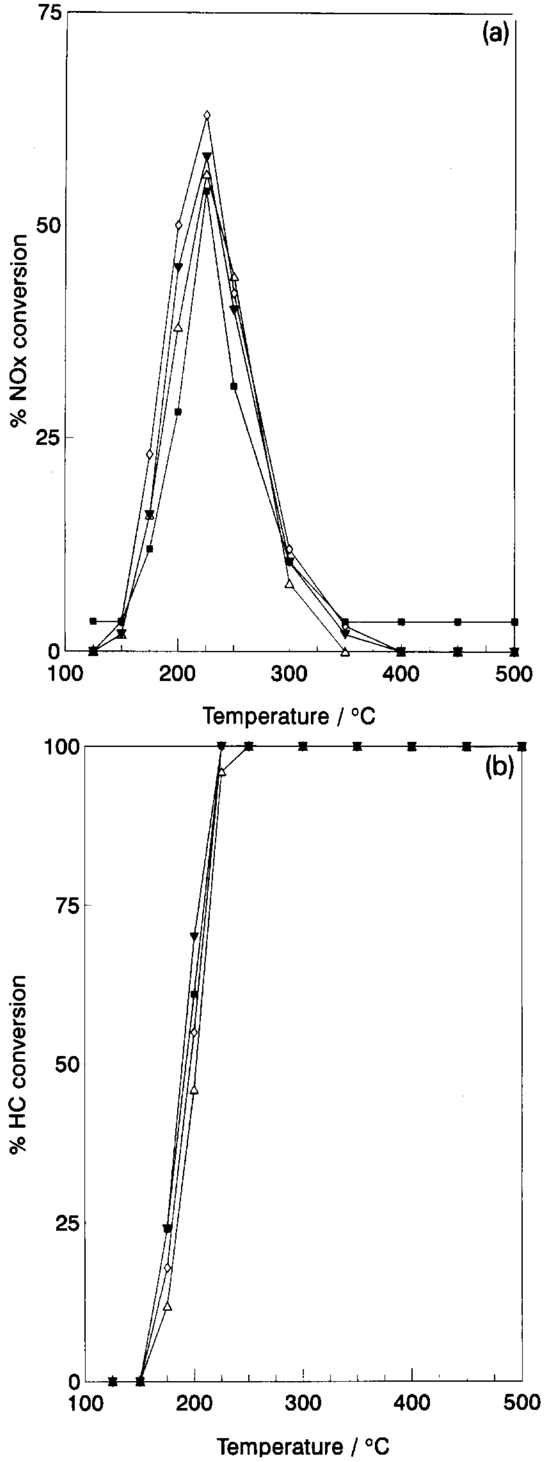

Fig. 2. (a) NO_x and (b) HC conversion as a function of temperature using olefinic hydrocarbons on a Pt catalyst: (▲) ethene, (▼) propene, (◇) 1-butene, (△) 1-octene.

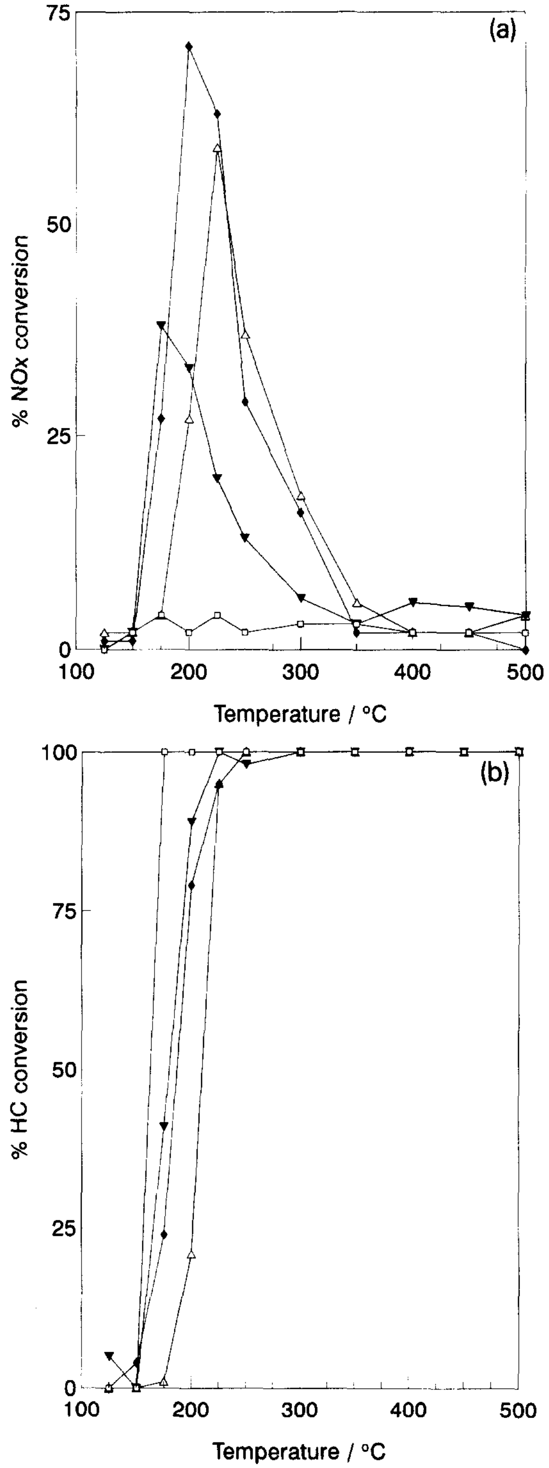

Fig. 3. (a) NO_x and (b) HC conversion as a function of temperature using alcoholic hydrocarbons on a Pt catalyst: (□) methanol, (▼) ethanol, (◆) 1-propanol, (△) 1-butanol.

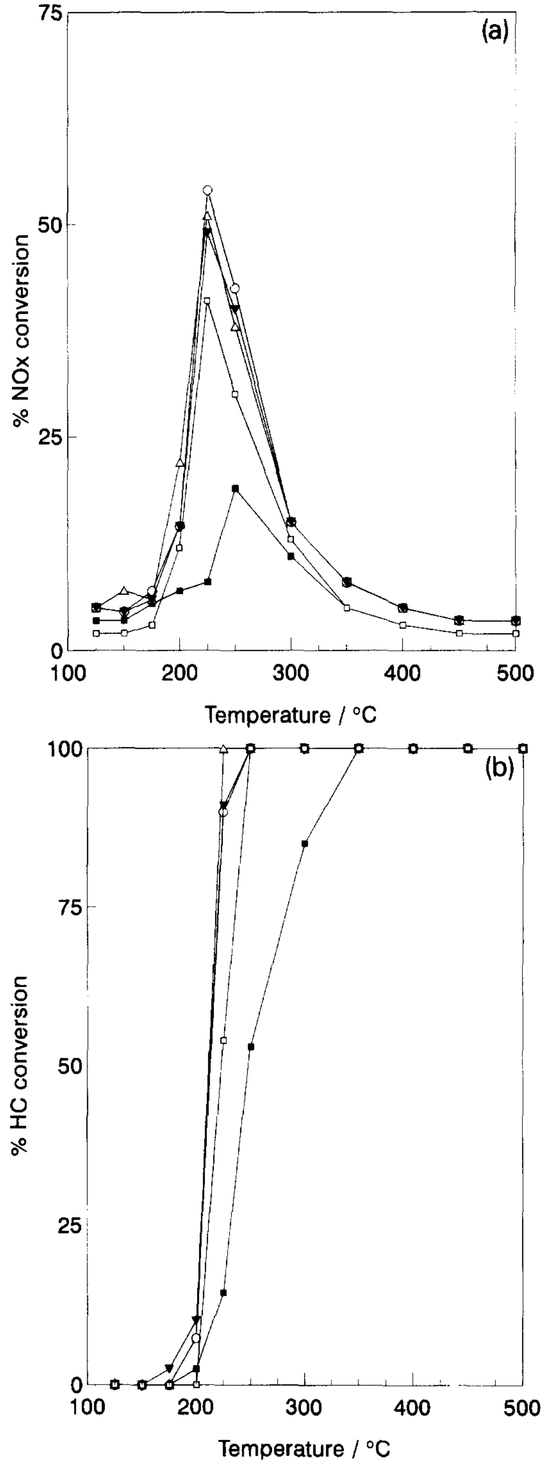

Fig. 4. (a) NO_x and (b) HC conversion as a function of temperature using aromatic hydrocarbons on a Pt catalyst: (□) toluene, (▼) 1,2-xylene, (○) 1,3-xylene, (△) 1,4-xylene, (■) 1-methylnaphthalene.

tical properties. Curiously, the branched paraffin, 2,2,4-trimethylpentane, is less effective than either. However, all these compounds are much more effective than, for example, butane or propane.

Fig. 2a and Fig. 2b show that olefinic compounds are much more effective than paraffinic compounds and show high activity and selectivity at low temperatures. For example, ethene is almost equally as effective as 1-octene, with both showing NO_x conversions of over 50% at 225°C. Alcohols (see Fig. 3a and Fig. 3b) are also very effective reductants, with the maximum NO_x conversion being over 70% for 1-propanol and 1-butanol, around 40% for ethanol, but almost zero for methanol. Aromatic compounds (see Fig. 4a and Fig. 4b) show moderate NO_x conversion with the various xylenes being most effective, followed by toluene. Curiously, 1-methylnaphthalene is rather ineffective, possibly because it is not a sufficiently good reductant for oxygen adsorbed on Pt. Note that the oxidation of 1-methylnaphthalene is significantly less facile than that for any of the other aromatic compounds.

Overall, these results show that for a specific carbon number the order of efficiency increases in the order isoparaffins < aromatics < n-paraffins < olefins = alcohols.

We have also investigated the NO_x reduction reaction on various supported platinum group metal catalysts [10–12] and while there are similarities to some of the published work from other groups there are also some significant differences which need to be considered. Fig. 5 compares the activity 1% loading alumina-supported catalysts as a function of temperature (test conditions: 500 ppm NO, 1000 ppm propene, 5% oxygen, total flow-rate 2000 cm^3 min^{-1} $gcat^{-1}$). These results confirm the results from other published work summarised in Table 1, namely the relatively high activity of Pt even at low temperatures, and the comparatively low activity of Pd, Rh, and Ir. Note also the different temperature ranges over which these different catalysts are effective in NO reduction.

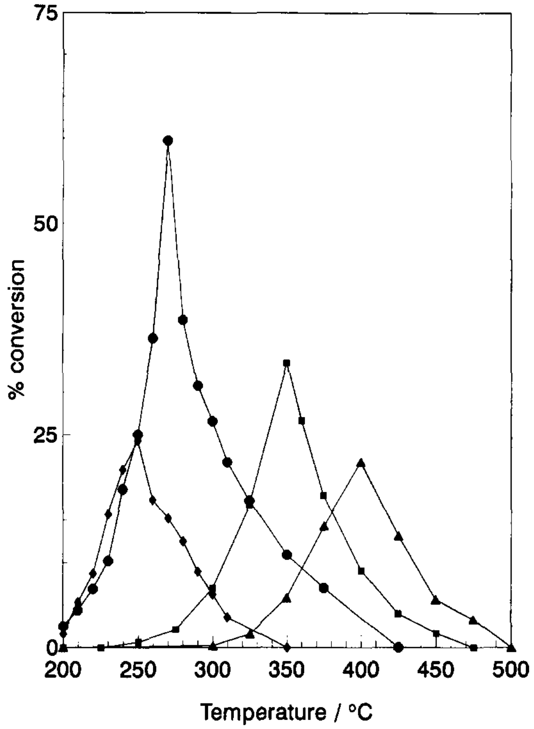

Fig. 5. NO_x reduction as a function on temperature on 1% PGM/ Al_2O_3 catalysts: (●) Pt, (◆) Pd, (■) Rh, (▲) Ir.

The onset of NO reduction and the peak in the NO conversion are closely related to the oxidation of propene as shown in Fig. 6. In all cases the reduction of NO begins at the same time as the oxidation of propene. The two conversions then tend to rise together until the NO reduction reaches a maximum close to the temperature at which the propene oxidation is complete. There seems to be a clear link between the capacity of propene to reduce the catalyst and the activity for NO removal.

This relationship between the NO reduction and the propene oxidation is largely responsible for the trend in NO_x conversion with Pt metal loading shown in Fig. 7. (The propene oxidation curves are omitted for clarity but in each case they parallel the rise in NO conversion.) As the metal loading is increased the activity per gramme of catalyst increases and so the oxidation of propene sets in at progressively lower temperatures. A parallel increase in the activity for NO reduction means that this reaction also commences at lower temperatures as the Pt loading is increased. Thus for

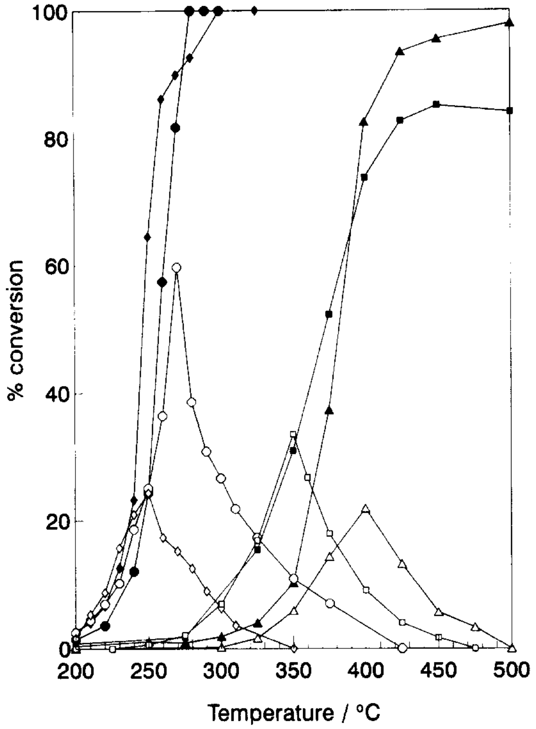

Fig. 6. Coincidence of NO_x reduction and C_3H_6 combustion on PGM/ Al_2O_3 catalysts: (●) Pt, (◆) Pd, (■) Rh, (▲) Ir, (open) NO_x, (closed) C_3H_6.

a 2% Pt catalyst the reaction starts below 200°C and peaks at around 250°C, whereas with a 0.1% Pt catalyst there is no detectable conversion below 250°C and the peak is at about 350–370°C.

The increase in the activity for the NO reduction with increasing Pt content is not simply related to the change in the Pt metal area. The catalysts with higher Pt loadings contain only a proportionately larger amount of Pt metal area (i.e. the 2% catalyst has about 4 times the Pt area of the 0.5% catalyst) whereas the increase in activity at the lower temperature is very much greater than this. There appears to be a particle size effect with larger Pt particles having significantly higher turnover frequencies. This will be considered again later.

The conversion of NO continues above the peak maximum temperature, but NO_2 becomes the predominant product. This is easily explained because the peak maximum in NO conversion corresponds quite closely to the temperature at which the combustion of the propene is complete. In fact, in other unpublished work [13] we have found that even though the gas mixture may contain some unburnt hydrocarbon there will be some surface sites which remain fully oxidized and so the formation of NO_2 can begin before the complete removal of the propene. Eventually, the formation of NO_2 is the only NO reaction observed and the amount of NO_2 formed is limited only by the thermodynamic equilibrium.

The effect of changing the oxide support on the activity of the Pt for the propene/NO/O_2 reaction has been investigated by several groups (see Table 1 and Fig. 8 and Fig. 9). In the work of Zhang et al. [3] changing from $AlPO_4$ to $AlPO_4$–SO_4 results in an increase in the overall conversion of NO. Interestingly this change of support also leads to a decrease in the selectivity for the formation of N_2O. This result is difficult to understand but could be potentially very important since SO_2 is often a component of an exhaust gas and could deposit as a sulphate on an alumina-based support. If such deposits actually enhanced the activity for NO reduction and at the same time

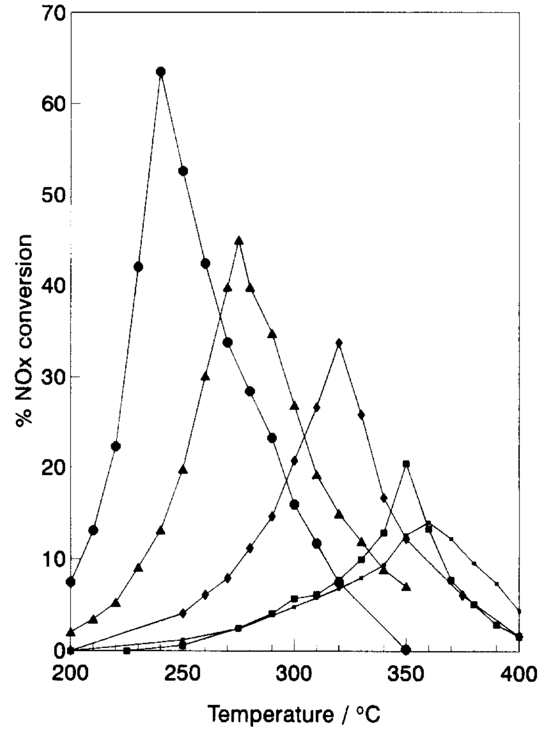

Fig. 7. NO_x reduction as a function of temperature on Pt/Al_2O_3 catalysts with different metal loadings: (●) 2% Pt, (▲) 1% Pt, (◆) 0.5% Pt, (■) 0.25% Pt, (■, small) 0.1% Pt.

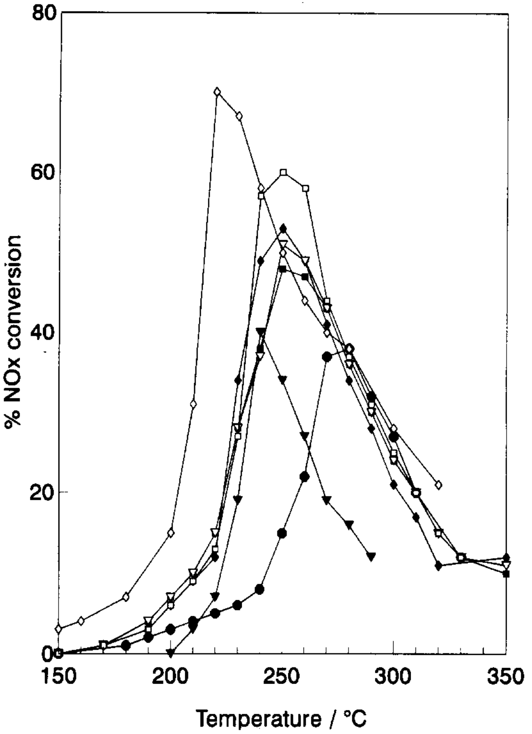

Fig. 8. NO_x reduction as a function of temperature on different metal-oxide supported Pt catalysts: (□) Pt/Al_2O_3, (◇) Pt/SiO_2, (▽) Pt/ZrO_2, (●) Pt/TiO_2, (■) Pt/SnO_2, (◆) Pt/WO_3, (▼) Pt/MgO.

reduced the selectivity for the formation of N_2O this would be very useful. However, Xue et al. [14] have reported that SO_2 inhibits the oxidation of NO to NO_2 so if this is a key step in NO reduction it would be expected that SO_2 would inhibit this reaction also.

Hamada [5] finds only small effects of changing from alumina to silica with his Pt catalysts. Table 1 shows that the silica-supported catalyst is somewhat more active than the corresponding alumina-supported catalyst and also perhaps less selective for the formation of N_2O.

Fig. 8 shows the variation in the activity for the NO reduction reaction on various metal oxide-supported 1% Pt catalysts from our own work. Fig. 8 shows that many of the catalysts have very similar activities (approximately 50% NO conversion at 250°C). These include: alumina, zirconia, tin(IV) oxide and tungsten(VI) oxide. The 1%Pt/TiO_2 is less active and the peak maximum occurs at a higher temperature, whereas the 1%Pt/SiO_2 is more active and has a maximum conversion at a lower temperature. Although 1%Pt/MgO is active for both NO reduction and propene oxidation at 250°C, it is considerably less selective for NO reduction than any of the other catalysts which are active at this temperature.

Fig. 9 shows the propene oxidation profiles corresponding to the NO reduction curves in Fig. 8. The coincidence between the onset of NO reduction and the onset of propene oxidation is again very noticeable.

When the peak activity in the NO conversion profiles is plotted against the temperature of this peak maximum the plot shown in Fig. 10 is obtained. These results show that for a particular set of experimental conditions (space velocity, gas composition) there is an upper limit to the NO_x conversion at any temperature. Presumably this reflects changes in the relative rates of the propene/NO and propene/O_2 reactions, or in the relative rates of reoxidation of Pt by NO or O_2, as the temperature is varied. These results suggest

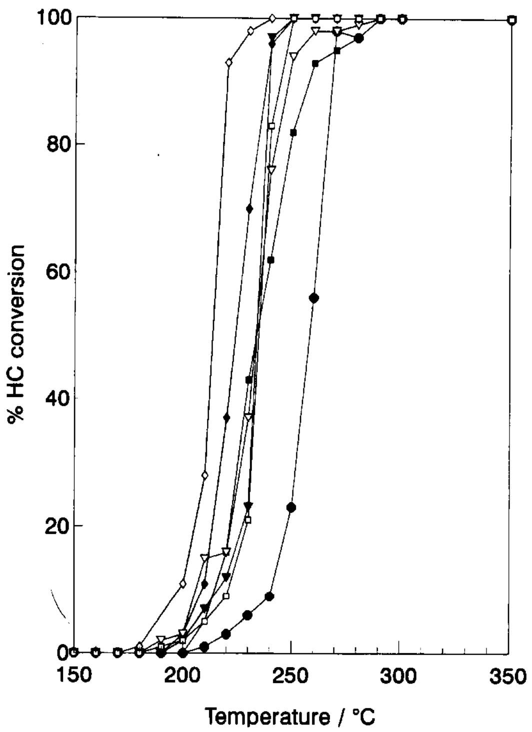

Fig. 9. C_3H_6 combustion as a function of temperature on different metal-oxide supported Pt catalysts: (□) Pt/Al_2O_3, (◇) Pt/SiO_2, (▽) Pt/ZrO_2, (●) Pt/TiO_2, (■) Pt/SnO_2, (◆) Pt/WO_3, (▼) Pt/MgO.

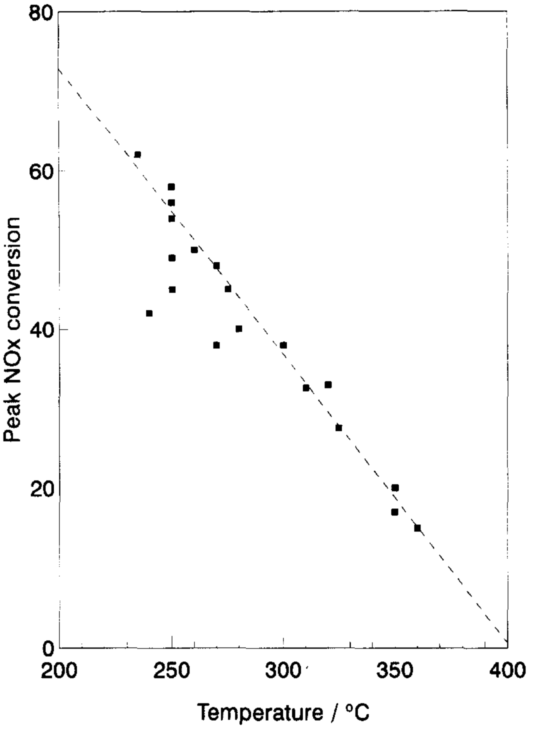

Fig. 10. Variation of peak NO_x reduction with temperature for a range of supported Pt catalysts (dotted line shows trend for Pt/Al_2O_3 catalysts).

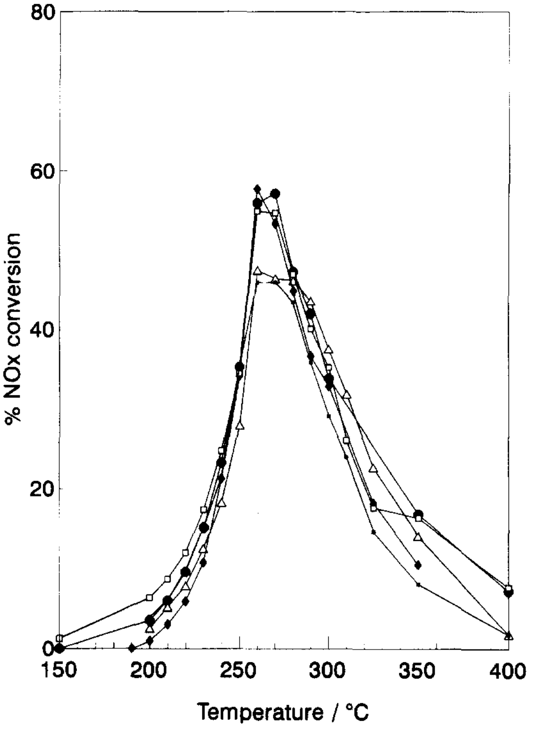

Fig. 11. Effect of metal dispersion on NO_x reduction activity for Pt/Al_2O_3 catalysts: (△) 4.6%, (□) 6%, (●) 9%, (■) 42%, (◆) 82%.

that unmodified Pt catalysts are likely to be limited in their capacity to selectively reduce NO in this temperature range. The real challenge will be to find ways of promoting the Pt to obtain a conversion above the limit seen in Fig. 10.

It has been noted above that there may be a small particle size effect because the increase in activity with Pt loading was larger than would be expected from the increase in Pt metal area. To investigate this, further series of alumina- and silica-supported Pt catalysts were prepared in which the average Pt particle size was adjusted by varying the calcination time (1–24 h) and temperature (500–700°C) for samples from a single batch of each catalyst. The effect of Pt dispersion is shown for the alumina-supported and the silica-supported catalysts in Fig. 11 and Fig. 12, respectively. From the results available it appears that there is little effect of metal dispersion for the alumina-supported catalysts over the range of average Pt particle sizes from 2.7 to 25 nm. In contrast, the Pt/SiO_2 catalysts do show some sen-

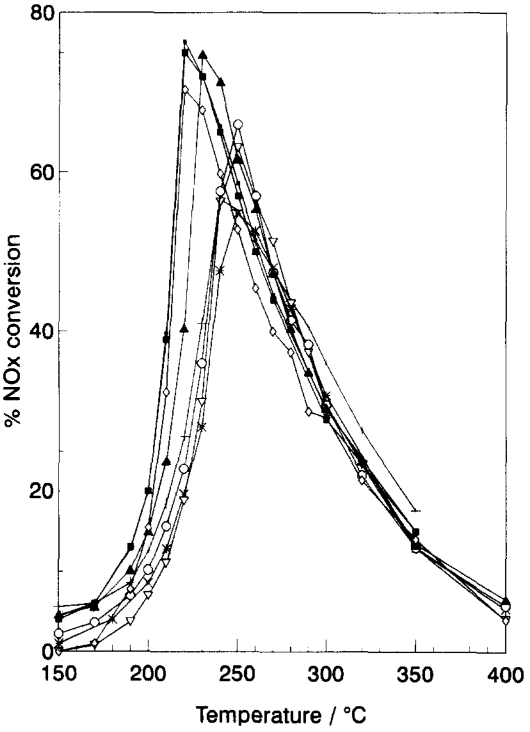

Fig. 12. Effect of metal dispersion on NO_x reduction activity for Pt/SiO_2 catalysts: (∗) 1.8%, (+) 3.5%, (▽) 4.5%, (○) 6.5%, (▲) 9%, (◇) 22%, (■) 35%, (■ small) 39%.

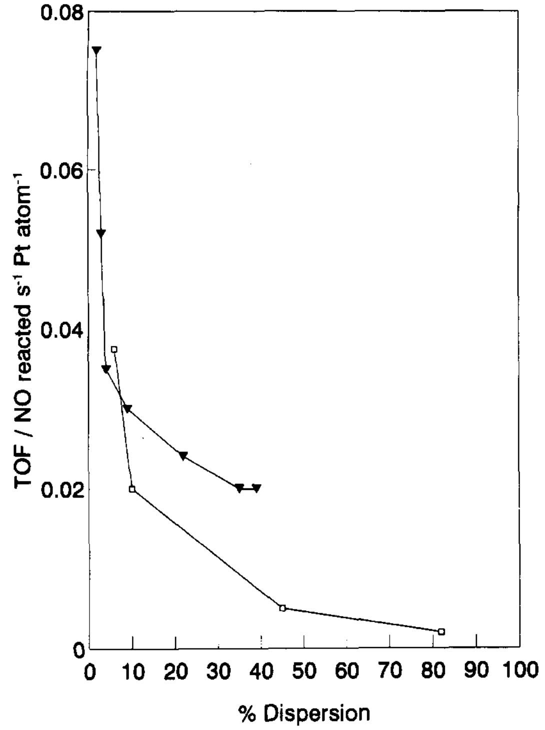

Fig. 13. Turnover frequency as a function of platinum dispersion: (▼) Pt/SiO_2 at 210°C, (□) Pt/Al_2O_3 at 230°C.

sitivity to platinum dispersion. On decreasing the dispersion from 39% to 1.8% (average Pt particle size increasing from 2.9 to 63 nm), the maximum NO conversion falls from about 80% to 50% and the temperature at which the maximum activity is seen moves from 210 to 250°C. However, the change in Pt surface area is much larger than this change in activity.

This is best seen in Fig. 13 which shows calculated turnover frequencies (TOF) for the two sets of catalysts at temperatures at which the conversion is well below the maximum. These results show that the TOFs for catalysts with 10% metal dispersion (corresponding to an average particle size of 11 nm) are approximately twice those of catalysts with 40% dispersion (3 nm). Below 5% dispersion (23 nm) the TOF increases rapidly indicating that very large particles have a high specific activity. However, it should be noted that the increased activity per surface atom at low dispersion is offset by the decrease in the number of surface atoms as the average size of the metal particles increases.

Metal particle size effects are thus quite important. From studies of the reduction of NO by hydrogen and carbon monoxide over supported platinum group metal catalysts, Otto and Yao [15] and Kašpar et al. [16] have concluded that metal atoms in a particulate phase are more active than atoms in a dispersed phase and that NO dissociation is promoted by an increase in particle size. From the reduction of NO by methane on Pt/Al_2O_3, Demicheli and co-workers have shown that specific reaction rate (or turnover frequency) increases with increasing particle sizes from 1.5 to 15 nm [17]. Xu and Goodman [18] have reported that with palladium catalysts the metal particle size affects the selectivity of NO decomposition or reduction to N_2 and N_2O: N_2O is not formed on small particles (<5 nm).

The comparison between alumina- and silica-supported catalysts has been extended to Pd and Rh. Fig. 14 shows the NO conversion versus temperature for these catalysts (the Pt results are included again for ease of comparison). The

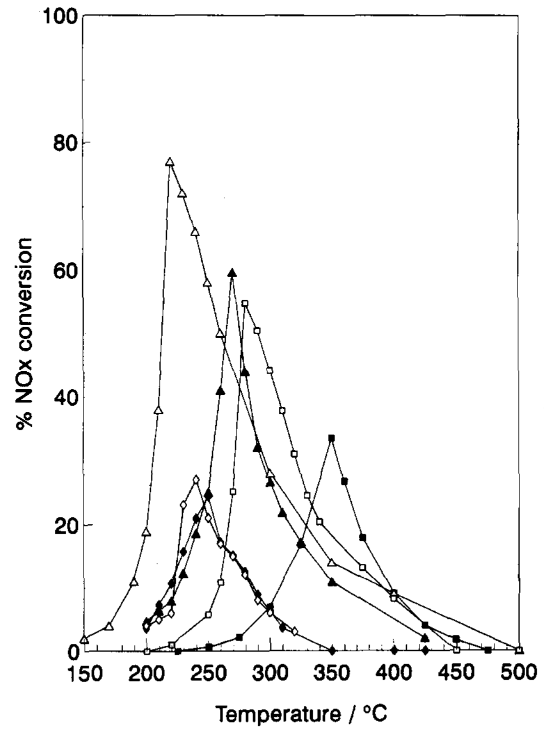

Fig. 14. NO_x reduction as a function of temperature for PGM catalysts: (▲) Pt/Al_2O_3, (△) Pt/SiO_2, (■) Rh/Al_2O_3, (□) Rh/SiO_2, (◆) Pd/Al_2O_3, (◇) Pd/SiO_2.

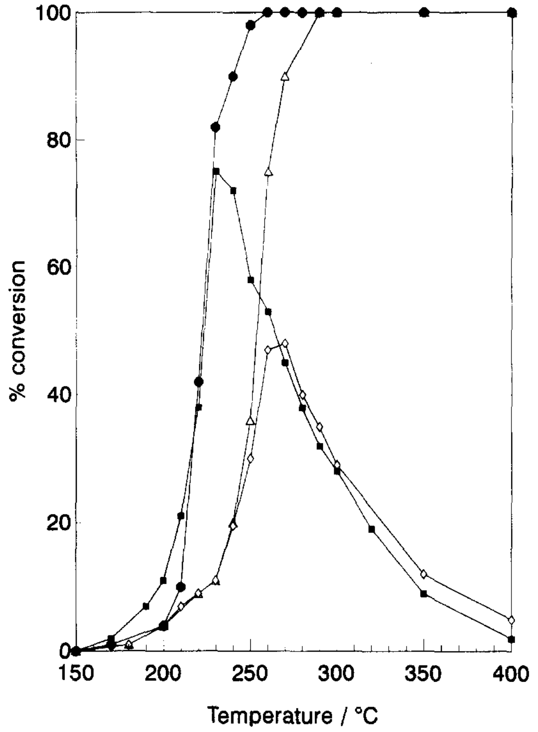

Fig. 15. NO_x reduction and C_3H_6 oxidation as a function of temperature for Pt catalysts with 10% metal dispersion: (■) Pt/SiO_2 (NO_x), (●) Pt/SiO_2 (HC), (◇) Pt/Al_2O_3 (NO_x), (△) Pt/Al_2O_3 (HC).

results show that for each of the metals, silica-supported catalysts are more active than those on alumina, although with Pd the difference is rather small. The metal dispersions (Pt/Al_2O_3, 41%; Pt/SiO_2, 35%; Pd/Al_2O_3, 28%, Pd/SiO_2, 19%; Rh/Al_2O_3, 51%; Rh/SiO_2, 49%) are sufficiently close, given the small effect of particle size in this range noted above, that this would not, by itself, account for the higher activity of the silica-supported catalysts. These results are somewhat at odds with those reported by Hamada [5] who, for example, found that Rh/Al_2O_3 was much more active than Rh/SiO_2. We do not have an explanation for these differences in relative activities but the sensitivity of the NO reduction reaction to experimental conditions may be a contributing factor.

In order to more closely compare the activities of alumina- and silica-supported catalysts, two sets of catalysts were prepared from the 1% Pt samples by adjusting the calcination treatment so as to obtain catalysts on each support having dispersions of ca. 10% and ca. 40%. The activity/temperature profiles for the 10% dispersion catalysts are shown in Fig. 15 and for the 40% dispersion catalysts in Fig. 16. The silica-supported catalysts are clearly more active in both cases. Consequently, there is a real support effect although whether this is a primary effect — the support is directly involved in the reaction — or a secondary support effect — the support modifies the true *active* phase — is not clear. It is certainly possible that Pt particles on the two supports could have different morphologies and this could account for differences in activities if, for example, the reaction proceeds more rapidly on smooth surfaces.

Another interesting feature of these catalysts is their activity for the oxidation of propene in the presence and in the absence of NO. Fig. 17 shows these results. In the absence, or in the presence of NO, the silica-supported catalyst is considerably

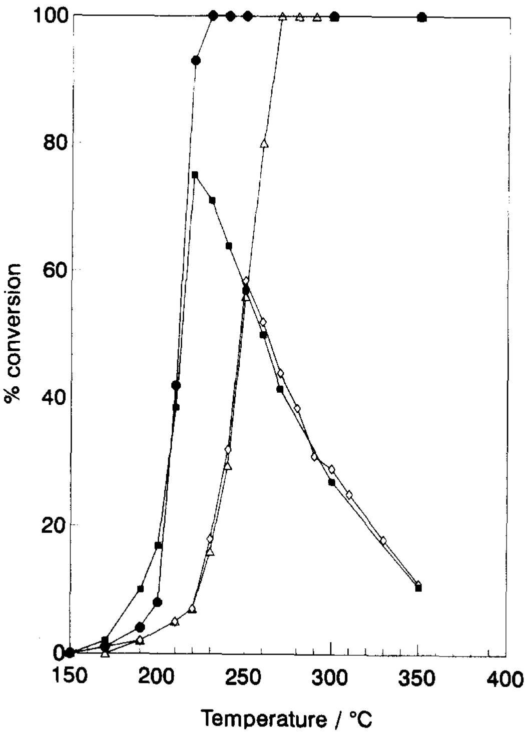

Fig. 16. NO_x reduction and C_3H_6 oxidation as a function of temperature for Pt catalysts with 40% metal dispersion: (■) Pt/SiO_2 (NO_x), (●) Pt/SiO_2 (HC), (◇) Pt/Al_2O_3 (NO_x), (△) Pt/Al_2O_3 (HC).

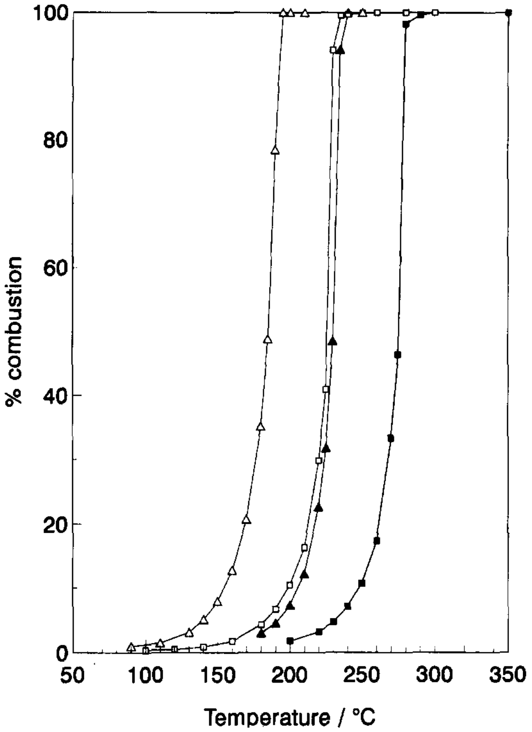

Fig. 17. C_3H_6 oxidation as a function of temperature in the presence and absence of NO: (□) Pt/SiO_2 with NO, (△) Pt/SiO_2 without NO, (■) Pt/Al_2O_3 with NO, (▲) Pt/Al_2O_3 without NO.

more active with the reaction commencing at a temperature about 50°C lower. More interestingly, however, is the fact that when NO is present, even at a much lower concentration than the O_2, the oxidation of propene is seriously inhibited, the temperature for any particular percentage conversion increasing by about 50°C. These results seem to suggest that even though the dissociative adsorption of oxygen is expected to be very fast under these experimental conditions and so the adsorption of NO would be expected to be very inhibited, there is a strong interaction (competition?) between oxygen and NO for surface sites. The oxidation of an alkene is normally so facile that it is possible that reoxidation, or perhaps, more likely, desorption of H_2O from surface sites is rate determining. (The two steps are, of course, interdependent since readsorption of oxygen cannot occur until OH groups are removed from the surface.) If NO adsorption could inhibit either of these desorption/readsorption steps it would account for the lower activity for propene combustion.

This possibility raises an interesting point concerning the mechanism of NO reduction on Pt under lean-burn conditions and this will be addressed more fully below. However, it is worth raising the question here as to whether the adsorption of NO in competition with O_2 is facilitated by the surface OH groups which must be present in a steady state equilibrium with the gas phase. Dümpelmann et al. [19] have recently discussed the enhancement of the reaction between NO and CO by hydrogen and water over Pt-containing catalysts. Although their work is concerned with conventional stoichiometric reaction conditions, there is possibly a similarity to our own work under lean-burn conditions. In their work, although they do not arrive at a clear explanation, they demonstrate that the addition of hydrogen or water to a stoichiometric mixture of CO and NO can significantly enhance the conversion of both NO and CO. One suggestion they make is that NO dissociation is hydrogen assisted, e.g.,

$$NO(g) + {*H} = {*N} + {*OH}$$

Under our lean-burn conditions it might be more appropriate to write this in the form:

$$NO(g) + {*OH} = {*N} + {*H_2O} = {*N} + H_2O(g)$$

or even as a non-dissociative adsorption, given the comparatively low temperatures in our experiments:

$${*NO} + {*OH} = {*NO*OH}$$

Such a species could explain the inhibition of propene oxidation by limiting the amount of available active sites ($Pt–O_s$) while at the same time being consistent with the fact that no NO_2 is observed when there is propene in the gas mixture. Another fact that may support this suggestion of enhanced adsorption of NO when OH is present is that with conventional hydrocarbon combustion catalysts water is a severe poison especially at the temperatures used in our NO reduction experiments. Thus, we have shown elsewhere [20] that the rate determining step in methane oxidation is

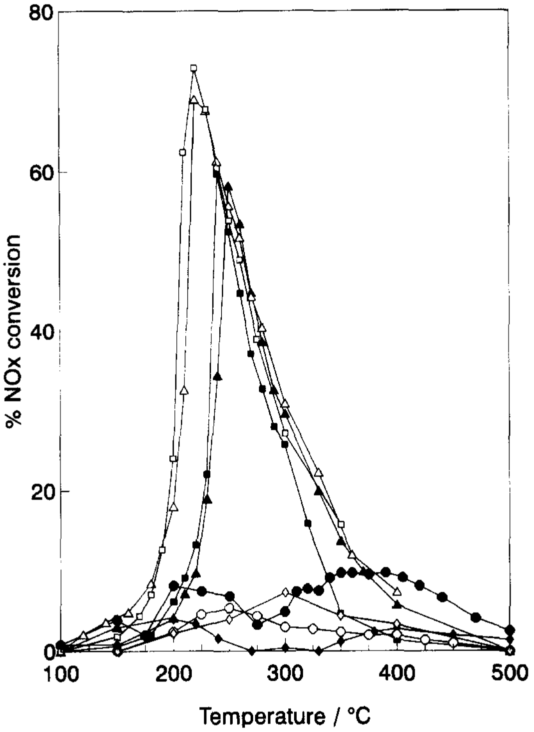

Fig. 18. NO_x reduction as a function of temperature using different hydrocarbons: (□) C_2H_4, (◇) C_2H_6, (△) C_3H_6, (○) C_3H_8, (open) Pt/SiO_2, (shaded) Pt/Al_2O_3.

probably *not* the breaking of the first C–H bond but rather the desorption of product H_2O. It seems that surface OH groups are quite stable on the surface of platinum group metals at temperatures below about 250°C. The implications of these various results in terms of the mechanism of NO reduction under lean-burn conditions will be assessed later.

The effect of changing the hydrocarbon in the NO reduction has been examined. Table 1 summarises some published results for the NO/propane reaction. In all cases the activity is low and only becomes significant at higher temperatures. Clearly propane is much less effective than propene. This has also been established by Engler et al. [7] as illustrated above in Fig. 1a. In our own work we have compared the effectiveness of ethene, ethane, propene, and propane using equivalent concentrations of carbon (1500 ppm of C_2 compounds, 1000 ppm of C_3 compounds) for both silica- and alumina-supported Pt catalysts. Fig. 18 shows that both alkenes give high NO conversion and in each case the Pt/SiO_2 catalysts is more active than the Pt/Al_2O_3 catalyst. Hydrocarbon combustion is coincident with NO reduction and no NO_2 is formed until after the peak in NO conversion. By contrast, both alkanes with either catalyst show only poor NO reduction activity. The 'light-off' of hydrocarbon oxidation occurs at a higher temperature than with alkenes and is less steep, reflecting the greater difficulty in activating the saturated compounds.

Hamada [5] has noted the influence of water on the NO reduction reaction using propane: the NO/propene reaction is not affected by water. He proposes that this means that the activity of noble metal/alumina catalysts for NO reduction by propane may be due to a cooperative effect between the noble metal and alumina. He suggests that the fact that water vapour does not inhibit the propene/NO reaction but does affect the propane/NO reaction supports this model. He envisages that the water inhibition effect can be ascribed to the inhibition of a reaction step on alumina leading to N_2 formation. This is a reasonable suggestion, but an alternative model can be proposed. From our work on the combustion of saturated hydrocarbons [21] we have also noted a strong inhibition of hydrocarbon oxidation by water vapour. However, this has been attributed to a shift in the equilibrium from metal oxide (or chemisorbed oxygen), which comprises active sites for C–H bond activation in saturated hydrocarbons, to metal hydroxide (or surface adsorbed OH groups) which are inactive sites for C–H bond activation. There is independent structural evidence for equilibria of this type:

$$\underset{\text{(active)}}{MO} + H_2O = \underset{\text{(inactive)}}{M(OH)_2}$$

This provides an alternative explanation of the water inhibiting effect for NO/saturated hydrocarbon reactions on alumina-supported platinum group metal catalysts.

With the alkanes, NO_2 formation is observed from relatively low temperatures (> 100°C) and, therefore, not just after the complete combustion of the hydrocarbon. Clearly NO can react with adsorbed oxygen on Pt at these low temperatures so the fact that it is not observed in the NO/propene reactions needs to be explained. One possibility is that in the presence of propene any NO_2(ads) formed is reduced back to NO before it can desorb, or any NO_2 which does desorb reacts rapidly with any adsorbed hydrocarbonaceous moieties formed in the adsorption of propene and is again reduced back to NO. Since we do not detect N_2 at these low temperatures there does not seem to be a direct route to N_2 from NO or NO_2 under these conditions which might explain the absence of NO_2 formation when propene is present.

3. Mechanistic studies

There have been a number of studies in which the mechanistic aspects of the NO reduction reaction have been considered but as yet there is little definitive evidence in support of one model rather than another and as a consequence several mechanisms have been proposed. As summarised by Hamada [5] these can be subdivided into decomposition mechanisms and reduction mechanisms, although as we shall see later the dividing line between these two categories is very unclear. On the basis of his results he does not arrive at a definitive mechanism but lists the three important factors for the selective reduction of NO to occur. These are: activation of the hydrocarbon; activation of oxygen; selective reaction of an intermediate with NO_x in preference to oxygen.

Zhang et al. [3] speculate that an important role of oxygen with Pt catalysts is to activate the hydrocarbon. Based on results for the oxidation of propene in the absence and in the presence of SO_2 they conclude that it is likely that the selective reduction of NO proceeds via NO_2 followed by the reaction of NO_2 with oxygen-activated hydrocarbon. They suggest that the large amount of NO_2 formed in the propene/NO/O_2 reaction over Pt catalysts also supports this speculation. The formation of N_2O is inhibited by SO_2 which they attribute to the retarded mobility of adsorbed NO in the presence of SO_2.

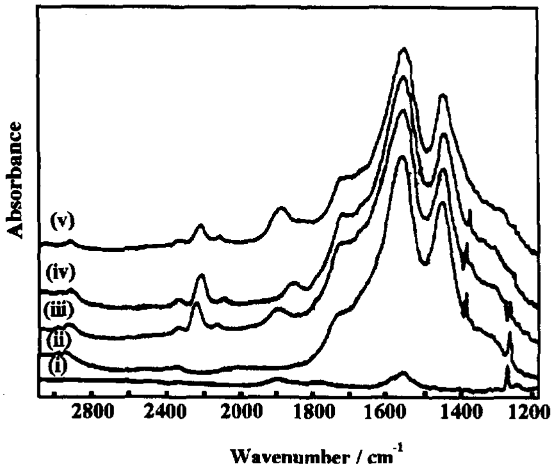

Fig. 19. IR spectra of adsorbed species on Rh/Al_2O_3: (i) after addition of ^{14}NO, (ii) after addition of $C_3H_6+O_2$, (iii) after addition of $^{14}NO+C_3H_6+O_2$, (iv) after addition of $^{15}NO+C_3H_6+O_2$, (v) after cutting $C_3H_6+O_2$ from (iv).

Obuchi et al. [4] have given serious consideration to the mechanism of NO reduction. They associate the well established maximum in the NO reduction activity with increasing temperature with a mechanism in which a partially oxidised hydrocarbon, which may be carbonaceous radicals, are intermediates in reacting with NO or NO_x directly to produce N_2. They suggest that since the concentration of such carbonaceous intermediates will be temperature-dependent this could account for the maximum in NO conversion. At low temperatures the oxidation of the organic compound to form the intermediate does not occur at a substantial rate, whereas at high temperatures the complete oxidation of hydrocarbons proceeds too rapidly and so the concentration of partially oxidised intermediates decreases. Although not necessarily directly relevant to Pt-containing catalysts Obuchi et al. [8] have discussed the possible role of carbon deposits and show by electron spin resonance that carbonaceous radicals and reactive carbon deposits are formed on alumina in the selective reduction of NO by propene.

Bamwenda et al. [9] have undertaken an in situ FT-IR study of the NO/propene reaction over Rh/Al_2O_3 catalysts at 350°C. Their results are summarised in Fig. 19. On adding NO they see peaks which they attribute to $Rh(NO)^+$, $Rh(CN)$ and isocyanate (-NCO), the latter being adsorbed on the alumina support. These infrared peaks increase in intensity over a period of 50 minutes. Cutting off the NO causes the peak attributed to $Rh(NO)^+$ to decline in intensity within a few minutes, but the effect is reversed when NO is reintroduced. Cutting off the supply of propene/oxygen causes the intensity of the band attributed to $Rh(NO)^+$ to increase and a band attributed to Rh(NO) to appear and grow. The $Rh(NO)^+$ band decreases in intensity faster in propene than in O_2, which they take as evidence for an interaction between $Rh(NO)^+$ and propene. They suggest that isocyanate is an intermediate in the selective reduction of NO and propose a tentative set of reactions between adsorbed -NCO with gaseous and/or surface oxygen and NO as follows:

$$\text{-NCO} + O_2 = NO + CO_2$$

$$= NO_2 + CO$$

$$\text{2-NCO} + O_2 = N_2 + 2CO_2$$

$$\text{-NCO} + [O] = NO + CO$$

$$= N_2O + CO$$

$$= N_2O + CO + [O]$$

$$2 - NCO = N_2 + 2CO$$

The possible role of isocyanate-type species is difficult to assess. On Pt these would be expected to have a very short lifetime [22] but their spillover to supports, such as alumina, is well documented. The question then arises as to whether such species are formed on Pt fast enough, transferred to the support in sufficient quantity, and then react efficiently with, presumably NO_2, to generate N_2. Dümpelmann et al. [19] report that isocyanate species on alumina are readily hydrolysed by water to ammonia and this may open up an alternative route for the destruction of surface isocyanate species which would *not* lead to the formation of N_2.

Sasaki et al. [6] also favour a mechanism in which the partial oxidation of propane, in their case, is followed by reaction with NO or NO_2 to form N_2. They suggest a mechanism as follows:

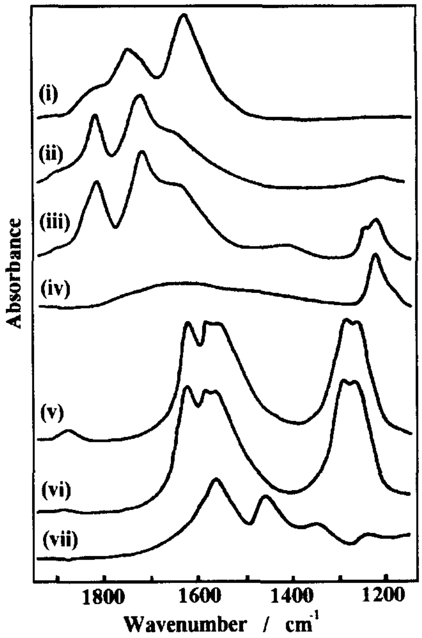

Fig. 20. IR spectra of adsorbed species on Rh/Al_2O_3: (i) after adsorption of NO on reduced Rh/Al_2O_3 (low dispersion), (ii) after adsorption of NO on reduced Rh/Al_2O_3 (high dispersion), (iii) after addition of NO + C_3H_6 at 180°C, (iv) addition of C_3H_6 after evacuation of (iv), (v) after adsorption of NO on oxidised Rh/Al_2O_3, (vi) after addition of C_3H_6 to (v), (vii) after heating (vi) to 225°C.

$$C_3H_8 + O^* = (C_pH_qO_r) + NO \ (\text{or } NO_2)$$

$$= N_2 + CO + H_2O$$

$$(C_pH_qO_r) + NO \ (\text{or } NO_2) = N_2 + CO + H_2O$$

$$(C_pH_qO_r) + O^* = CO_x + H_2O$$

Naito and Tanimoto [23] have performed a detailed set of infrared and isotopic labelling experiments on Rh/Al_2O_3 catalyst for the NO/propene/O_2 reaction. With this catalyst they find that the direct propene/O_2 reaction is slow at 180°C but is accelerated by addition of NO. In FT-IR experiments at room temperature (see Fig. 20) they find on exposing the freshly reduced catalyst to NO, bands at 1825 and 1730 cm^{-1}, which were assigned to linearly adsorbed Rh–NO, and a band at 1650 cm^{-1} which was attributed to the bent Rh–NO species. The relative intensities of these bands depended on the particle sizes of Rh metal, and linear NO(a) was abundant on highly dispersed catalysts. Addition of propene at room temperature had no effect on the spectra.

Addition of propene/NO at 180°C to the prereduced Rh catalyst led to the observation of bands at 1260 and 1230 cm^{-1}. After evacuation, it was found that adsorbed NO reacted slowly with propene when this was reintroduced in the gas phase. At 180°C the bands attributed to NO disappeared over a period of about 10 minutes with the formation of N_2 and N_2O.

When the Rh surface was precovered by adsorbed oxygen, by exposure to oxygen at room temperature, introduction of NO showed strong bands at 1620, 1590, 1560, 1290, and 1265 cm^{-1} which were assigned to the adsorbed NO_2(ads) or NO_3(ads) species. They suggested that a very weak band at about 1900 cm^{-1} may be attributed to $Rh–NO^+$. After evacuation of the gas phase NO at room temperature, propene was introduced and the temperature raised. These infrared bands only began to disappear above 225°C, which was taken to indicate that they are species at the vicinity of the alumina support.

The adsorbed state of propene was probed using microwave spectroscopy to analyse the various deuterated products formed using mixtures of C_3H_6 and C_3D_6. H/D exchange was observed at -53°C, but on addition of NO the exchange reaction did not commence until around room temperature and the main product changed from being a mixture of propene-1-d_1 and propene-2-d_1, indicating a change of the reaction intermediate from a propenyl species to sigma-allyl by interaction with adsorbed NO. In the case of the C_3H_6–C_3D_6–NO–O_2 reaction, the exchange rate decreased by an order of magnitude and the distribution of products changed completely. The product distribution was the same as found in the absence of NO but the rate of exchange was much slower. It was suggested that the slower exchange rate may have been due to fast removal of adsorbed hydrogen by NO_2(ads) or NO_3(ads), which would shift the equilibrium for dissociative adsorption of propene.

They conclude that excess oxygen in the propene/NO reaction modifies the Rh surface to make it oxidative, and become one on which NO_2(ads) and NO_3(ads) may be formed and which may promote the dissociation of propene by the fast removal of hydrogen to leave irreversibly adsorbed propenyl species. N_2 and N_2O may then be formed by the reaction of weakly adsorbed $Rh–NO^+$ species with these propenyl species.

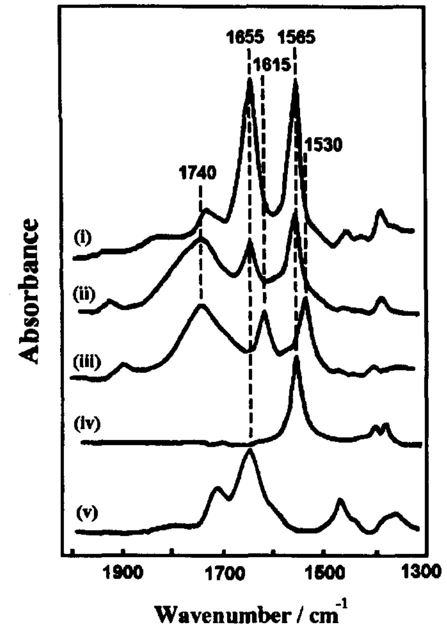

Fig. 21. IR spectra of adsorbed species on Pt/SiO_2: (i) after addition of $NO+C_3H_6+O_2$ at room temperature, (ii) after evacuation at 120°C after (i), (iii) after addition of $^{15}NO+C_3H_6+O_2$ followed by evacuation at 120°C, (iv) after addition of CH_3NO_2, (v) after addition of n-C_4H_9ONO.

Tanaka et al. [24] have performed detailed FT-IR studies on silica-supported Pt catalysts in an attempt to obtain information in support of their proposal that organo-nitro and organo-nitrite surface species are involved as intermediates in the selective reduction of NO by propene in excess oxygen. Their results are summarised in Fig. 21. Addition of propene/NO/O_2 at room temperature results in infrared bands at 1565 and 1655 cm^{-1}, which are attributed to $-NO_2$ and $-ONO$ groups in organo-nitro and organo-nitrite compounds, respectively. They compare these bands with characteristic absorbances for CH_3NO_2 at 1561 cm^{-1} and for n-C_4H_9ONO at 1658 cm^{-1}. Substitution of ^{14}NO by ^{15}NO confirmed that the bands were due to nitrogen-containing species. There was an additional band at 1740 cm^{-1} which did not respond to this substitution.

When either propene/NO/O_2 or propene/NO_2 was introduced to the Pt catalyst at 120°C a similar spectrum was obtained except that the band at 1730 cm^{-1} was now very small. This band, which had not responded to the substitution of ^{14}NO by ^{15}NO, was assigned to the –CO of an organic carbonyl species. It was assumed that Pt catalyses the conversion of the proposed organo-nitro or organo-nitrite species to the carbonyl species.

The reactivities of the three surface species (associated with the bands at 1565, 1655 and 1730 cm^{-1}) were examined by combining FT-IR and gas phase analysis. The bands attributed to the nitro and nitrite species decreased slowly under vacuum at 120°C, but the 1730 cm^{-1} band was unaffected. However, addition of gaseous NO_2 at this temperature resulted in a fairly rapid decrease in the intensity of the band at 1730 cm^{-1}. It was concluded, therefore, that the main NO reduction reaction takes place between carbonyl species and NO_2, resulting in the formation of N_2 and N_2O. A slower decline in the intensities of the bands at 1565 and 1655 cm^{-1} after introducing NO_2 lead to the suggestion that some, but not much, NO reduction may occur through a direct reaction with NO_2. In summary, they conclude that propene first reacts with nitrogen dioxide, which is formed from nitric oxide, resulting in the formation of nitro and nitrite species. Then the nitro and nitrite species partly change to carbonyl species at elevated temperatures and nitrogen and nitrous oxide are then formed mainly from reactions between nitrogen dioxide and these carbonyl species.

These authors have attempted to test out this hypothesis by investigating the reactivity of model compounds and comparing the results with the rate of NO reduction by propene on the same catalysts [24]. Oxidation of nitromethane and of n-butylnitrite gave products similar to that obtained in the propene/NO/O_2 reaction as far as the nitrogen-containing inorganic compounds was concerned. Finally, these authors note that although isocyanate species have been invoked by other authors, they find no evidence for infrared bands due to isocyanate species in their work.

Engler et al. [7] have undertaken a DRIFT experiment using a platinum-based catalyst and observed a strong band at 1787 cm^{-1} for a prereduced catalyst exposed at 225°C to a stream of NO. They conclude from this that adsorption of NO on Pt sites is a first crucial step for the reduction of nitrogen oxides.

These authors have also determined the product selectivity as a function of space velocity. From these results they have concluded that NO_2 and N_2 are probably primary products of the reaction, but N_2O is most probably a secondary product. They rationalize their observations by a sequence of elementary steps as follows:

$$NO + [S_1] = NO\text{-}[S_1]$$

$$NO - [S_1] + 1/2O_2 = NO_2\text{-}[S_1]$$

$$NO_2[S_1] = NO_2 + [S_1]$$

$$C_xH_y + zO_2 + [S_2] = C_xH_yO_{2z}\text{-}[S_2]$$

$$NO_2\text{-}[S_1] + C_xH_yO_{2z}\text{-}[S_2]$$

$$= 1/2N_2O + xCO_2 + yH_2O + [S_1] + [S_2]$$

$$NO\text{-}[S_1] + C_xH_yO_{2z}\text{-}[S_2]$$

$$= 1/2N_2 + xCO_2 + yH_2O + [S_1] + [S_2]$$

This proposed mechanism is highly speculative but may still contain elements which are relevant to the correct mechanism.

In our own work we have taken a different approach and have applied the technique of transient kinetic analysis to try to understand the mechanism of the selective reduction of NO on platinum-based catalysts. This work has been published elsewhere [10–12] and so only a brief account will be given here.

The basic technique which has been used is Temporal Analysis of Products (TAP). In this procedure it is possible to investigate reactions on a time-scale of milliseconds, and by using very small gas pulses of different compositions and separated by different time intervals it is possible to assess the extent to which different types of

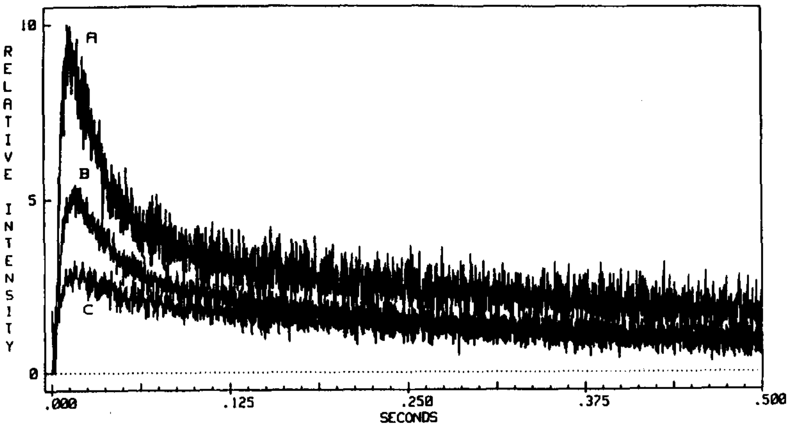

Fig. 22. Variation of N_2 yield with number of NO pulses over reduced Pt/Al_2O_3: (A) Average of pulses 1–10, (B) average of pulses 11–50, (C) average of pulses 51–90.

surface intermediate may be involved in the reaction.

Fig. 22 demonstrates that on a prereduced Pt/Al_2O_3 surface NO dissociation leads to the formation of N_2 but that the amount of N_2 formed decreases as the number of pulses of NO introduced is increased. It is easily shown that this self-poisoning is due to the retention of adsorbed oxygen, even at 400°C. Pulse-probe experiments in which adsorbed oxygen is removed by introducing a second pulse of either H_2 or CO immediately after the NO pulse show that the initial activity of the fully reduced Pt is completely stable providing all the surface adsorbed oxygen is removed between the successive NO pulses. Moreover, by adjusting the time interval between the introduction of the NO pulse and the pulse of reductant (CO or H_2) in the range 0.1–10 s, it is also possible to show that there is no *direct* interaction between the NO and the reductant.

Fig. 23 demonstrates this point for the NO–H_2 pump-probe experiments. It is seen that irrespective of the time interval between the two pulses the amount of N_2 produced is constant. Moreover, for the first experiment, where the time interval is only 0.1 s between the introduction of a pulse of H_2 and the subsequent introduction of the NO pulse, there is still some adsorbed hydrogen on the Pt when the NO pulse reaches the catalyst. Consequently, the fact that the amount of N_2 produced is the same as for an experiment where all the hydrogen has been desorbed, shows that there is no direct reaction between NO and adsorbed hydrogen on such fully reduced surfaces.

When these pulse-probe experiments are performed using propene and propene/O_2 mixtures

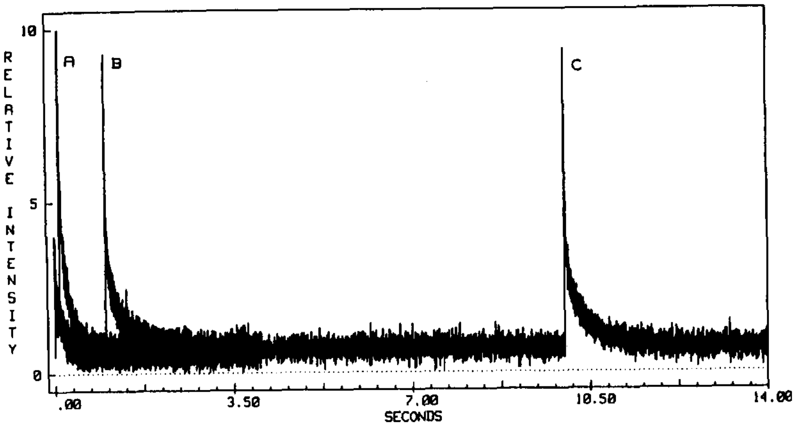

Fig. 23. Variation of N_2 yield with the interval between H_2 and NO pulses: (A) 0.1 s, (B) 1 s, (C) 10 s.

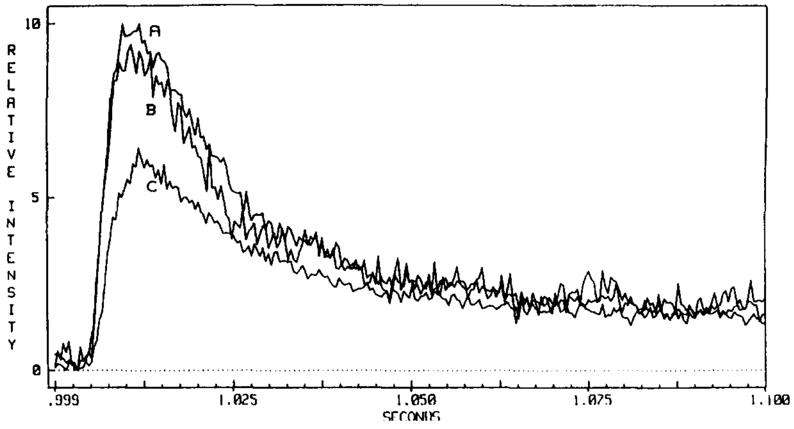

Fig. 24. Comparison of C_3H_6/O_2 and C_3H_6 alone as reductants of NO: N_2 yield for (A) equilibrium C_3H_6/O_2–NO, (B) C_3H_6–NO (average of first 10 pulses), (C) C_3H_6–NO (after 50 pulses).

as the 'reductant' two interesting features emerge as shown in Fig. 24. First, it is seen that the propene/O_2 mixture, even though this can be an overall *oxidising* mixture is effective at leaving the Pt surface active and stable for the conversion of NO to N_2. Second, when propene is used without O_2, the catalyst becomes self-poisoned due to deposition of carbonaceous material on the Pt. This would suggest that carbonaceous layers are not important in the selective NO reduction reaction on these catalysts. Moreover, it is possible that an important role of oxygen in the propene/NO/O_2 reaction is to prevent self-poisoning of the Pt by carbonaceous residues. Comparison between propene/O_2 and CO or H_2 as reductants (Fig. 25) shows that the propene/O_2 is rather better. The differences in the amount of N_2 produced are not great, but may be significant nevertheless in terms of the overall mechanism in a steady state kinetic experiment as compared to these transient conditions.

It is significant to note that when propene/O_2 pulses are followed by NO pulses a small, but significant amount of CO_2 is observed. This suggests that even under net oxidising conditions there is some tendency for carbonaceous species to become attached to the Pt. Possibly, therefore, under continuous flow conditions the lifetime of adsorbed propene species is quite long and sufficient to allow adsorption of NO at adjacent Pt sites.

The efficiency of CO or H_2 for NO reduction is completely eliminated when excess O_2 is introduced. This is easy to understand on the basis that an individual CO or H_2 molecule has insufficient reducing power to remove adsorbed oxygen as fast

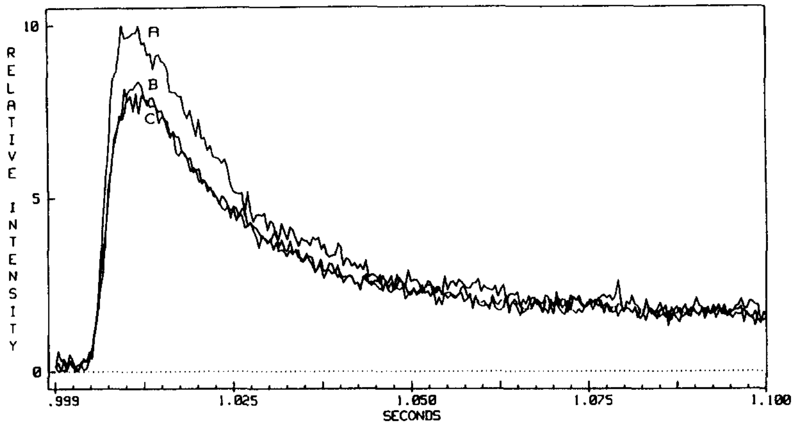

Fig. 25. Comparison of C_3H_6/O_2, CO and H_2 as reductants of NO: N_2 yield for (A) C_3H_6/O_2, (B) CO and (C) H_2.

as it is supplied by dissociative adsorption from the gas phase. Clearly, under these conditions the Pt remains in a more or less fully oxidised state and is totally inactive for NO reduction, producing instead NO_2. On the other hand, the fact that the propene/O_2 pulses leave the Pt in a state where a subsequent pulse of NO can be converted into N_2 shows that propene has sufficient reducing power to maintain some of the Pt in a reduced state even when the propene is mixed with an excess of O_2.

The TAP results indicate that two mechanisms may operate together for NO reduction. The first, and under our experimental conditions the most important, involves dissociative adsorption of NO on reduced Pt sites adjacent to adsorbed hydrocarbonaceous species derived from adsorbed propene, followed by desorption of N_2 and, through interaction with molecularly adsorbed NO, of N_2O. The second, involves a more specific interaction involving the hydrocarbonaceous species and is similar, but less specific, than that proposed by other workers who favour precisely defined intermediates such as isocyanates [22], or organo-nitro or organo-nitrite species [24]. In reality, the differences between these different models are a matter of degree and it seems entirely possible that under dynamic reaction conditions all may contribute to the overall selective NO reduction reaction. The relative importance of the various parts of the overall mechanism may vary from one catalyst to another, from one part of a Pt particle to another, and certainly as the experimental conditions (temperature, space velocity, gas composition) are varied.

It is recognised, of course, that our redox model has to account for the fact that a platinum surface exposed to a gas mixture containing a large excess of oxygen would be expected to become fully covered with a monolayer of oxygen essentially instantaneously, so the question arises as to whether under such circumstances there is any reasonable possibility that NO can get to the surface to become adsorbed and subsequently dissociated. The models proposed by Bamwenda et al. [9], Tanaka et al. [24], and Engler et al. [7], in a sense overcome this difficult by assuming that a specific intermediate (isocyanate, organo-nitro or organo-nitrite), or a specific interaction $\{NO_2\text{-}[S_1] + C_xH_yO_{2z}\text{-}[S_2]\}$ leads to the required selective reduction.

Our model really does not differ from these other models except in the strict description of the surface intermediate and the precise mechanistic steps which lead to NO dissociation and N_2 or N_2O formation. We envisage that NO is dissociated on the Pt surface at bare patches produced by removal of oxygen by propene. The adsorption of the NO will need to take place either at, on, or around the edge of the adsorbed propene on a patch of Pt atoms, otherwise the NO will simply be oxidised to NO_2, as indeed happens readily when there is no remaining propene. Therefore, the adsorption of NO is intimately connected to the hydrocarbon species on the surface. It is quite possible that the dissociative adsorption of NO can also be facilitated by having such species present on the surface when an NO molecule collides with it (note the work of Dümpelmann et al. [19]).

However, we do not see the need to propose any precisely defined surface species, such as isocyanate or organo-nitro or -nitrite species. Instead, in our model the organic compound has the simple role of maintaining a small patch of Pt atoms in a reduced state long enough for NO to be dissociatively adsorbed. It is recognised that for NO dissociation on Pt it may be necessary to have a large ensemble of Pt atoms — Masel and co-workers [25,26] have suggested an ensemble comprising 11 Pt atoms including step atoms. Such a large ensemble may not be required for small metal particles but this possibility cannot be excluded. Therefore, in our model it is necessary to take this into account. We suggest that the dissociative adsorption of NO is facilitated by the propene both in terms of creating reduced Pt sites and in terms of assisted adsorption. The propene on the surface continues to remove adsorbed oxygens from the Pt surface, and to prevent further adsorption of oxygen atoms by the simple expedient of converting these directly into CO_2. If an NO molecule approaches the Pt surface where there is a propene molecule undergoing complete oxidation there will be the enhanced possibility that the NO can be adsorbed and dissociated on the underlying Pt.

It is possible, of course, that a number of different pathways may be available essentially in parallel so that the approach of the NO to the Pt surface may also be intercepted and other surface species, such as isocyanate groups, or organo-nitro-type species, may be formed and could, indeed, be detected at lower temperatures by infrared spectroscopy. However, it is our view that such species, if they are formed, do not necessarily have any special role in NO reduction, and, more specifically, they do not have any precise composition or structure. We would envisage instead a general role for any hydrocarbonaceous species of (a) reduction of Pt, and (b) facilitating adsorption of NO. We would expect that any hydrocarbonaceous species of whatever composition and structure could be effective while it is still a coherent species, i.e., before it has been fully oxidised to CO_2 and H_2O. Clearly, some compounds will be more effective than others for the simple reason that they will have the optimum activity and reducing power. Compounds such as CO or CH_3OH, which are readily activated would be very effective except for the fact that their reducing power is inadequate to reduce the Pt for long enough to allow an NO molecule to access the Pt. Equally, compounds such as C_3H_8, are too difficult to activate and so although they have a large reducing power, they are only capable of reducing Pt at temperatures at which total oxidation is so favourable that NO has no opportunity to approach a reduced Pt site before this is reoxidised. Whether NO adsorption, dissociative or otherwise, is facilitated by adsorbed species, of which there may be a wide variety, is difficult to prove but would be consistent with emerging evidence of enhanced adsorption in other systems [27].

In summary, there seems little to be gained by trying to define the reaction scheme more precisely than is currently possible. The more important question which should be addressed is how can any of these models, all of which have common features, facilitate the design of improved catalysts. Can the reoxidation characteristics of Pt be modified, can the dissociative adsorption of NO be encouraged, can different sorts of carbonaceous residue be deposited and will this influence the overall activity and selectivity in the NO reduction reaction? These catalysts are a promising first step towards a successful selective NO reduction process under lean-burn conditions. But much further improvement is needed to overcome the inherent problems of platinum-based systems. For example, the activity/selectivity temperature 'window' is too narrow, and the formation of N_2O in substantial quantities is a major drawback. It is hoped that an assessment of the mechanistic features of these catalysts will eventually lead to ideas for the design and synthesis of improved catalysts having real commercial value.

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