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Low NO_x options in catalytic combustion and emission control

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Abstract

The options for preventing the release of nitrogen oxides into the atmosphere from combustion processes is considered both from the viewpoint on the one hand of using catalytic combustion to prevent the formation of nitrogen oxides and on the other of using hydrocarbons for the selective reduction of nitrogen oxides to nitrogen in the presence of excess oxygen. Combustion of methane at low temperatures on palladium-based catalysts is discussed, and some new results relating to the nature of the active catalyst and the rate determining step are presented. Current attempts to develop selective reduction catalysts for the removal of nitrogen oxides are summarised and the particular advantages and disadvantages of platinum group metal-based catalysts are discussed. The mechanism of the nitrogen oxide to nitrogen reaction is considered and some new results are presented which are consistent with a dissociative mechanism, possibly involving adsorbate-assisted dissociative adsorption of nitric oxide.

Keywords: NO_x options; Catalytic combustion; Emission control

1. Introduction

Nitrogen oxides (NO_x) are serious pollutants and legislation requires that the emission of NO_x is strictly limited. Most combustion processes result in the formation of NO_x, which may arise either from fuel-bound nitrogen or by nitrogen fixation in high temperature flames. It is difficult to prevent the formation of NO_x from fuel-bound nitrogen so that 'end-of-pipe' methods must be utilised to eliminate the pollution. Ammonia is well established as a selective reductant for NO_x in large scale stationary applications and Pt/Rh-based catalysts are widely used in mobile sources, such as gasoline engines operating close to the stoichiometric air/fuel ratio. Nitrogen fixation, on the other hand, can, in principle, be prevented by improving the control of the temperature in a flame since the reaction of N_2 only occurs at a significant rate at temperatures well above the average flame temperature. To some extent this can be achieved by redesign of the burner system, but for very low levels of NO_x emission catalytic combustion may provide an acceptable solution. In situations where catalytic combustion is not possible or not economic, alternative strategies must be adopted. Recently, there has been much interest in developing catalysts which will be selective for the reduction of NO_x in the presence of a large excess of O_2 (lean-burn conditions) where the reductant is a hydrocarbon

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rather than ammonia. A number of different systems have been studied, ranging from nonreducible oxides and zeolites, through base metal redox systems, to supported platinum group metals. In this paper we shall consider some fundamental aspects of the platinum group metal catalysts used for catalytic combustion and for the selective reduction of NO_x with hydrocarbons.

2. Catalytic combustion

In large scale (gas turbine) applications, where the demands on the catalysts in terms of activity and thermal stability are very severe, it is now well established that a staged combustion process is the most feasible [1]. As indicated in Scheme 1, catalysts are required both for low temperature lightoff and for high temperature combustion. With methane or Natural Gas as the fuel it is now accepted that Pd is the most active low temperature catalyst and, at present, mixed oxides (e.g., substituted barium hexaaluminates), such as those developed by Arai and colleagues [2], are the most stable and active high temperature catalysts. We shall concentrate here on the low temperature Pd catalysts.

Scheme 1. Outline of requirements for a catalytically stabilised thermal combustor (after [1])

Stage 1	start up flame (raises temperature to about 400°C)
Stage 2	low temperature catalyst (active at about 350°C and raises temperature to ca. 800°C)
Stage 3	high temperature catalyst (active at about 750°C and raises temperature to ca. 1200°C)
Stage 4	stabilised gas phase combustion (operates above ca. 1000°C and raises temperature to ca. 1500°C)

There has been a considerable amount of research on supported Pd catalysts for methane combustion but there is still uncertainty, for example, about the nature of the most active form of Pd, the influence of morphological effects, and the role of the support. An oxidised form of Pd is considered to be the most active state. However, since there appear to be several types of oxidised Pd there is still confusion about the optimum state. In recent years, there have been suggestions that highly dispersed PdO has a low activity [3], that larger PdO crystallites are the active phase [4–6], or that the optimum state corresponds to a skin of PdO on a Pd metal core [7,8]

Morphological effects have been invoked by Baldwin and Burch [4,5] to explain anomolous large enhancements in activity with time on stream. Similar effects have been claimed by Primet and co-workers [9–12] and Rodriguez et al. [13] have recently shown by in situ electron microscopy that PdO does undergo structural transformations in an oxygen-containing gas stream at 350°C, which is close to the temperature at which unusual catalytic activities have been observed. Garbowski et al. [11,12] have concluded on the basis of their electron microscopy investigations that the total oxidation of Pd to give bulk PdO is not a prerequisite for obtaining an active catalyst. They relate their results to a redox process involving surface metal atoms (Pd^0) and surface PdO, the extent of which is dependent on the morphology of the Pd metal particles. However, although morphological changes do occur, it is now also known that artefacts, such as the poisoning effect of chlorine, can complicate the interpretation of the kinetic results. [14] Indeed, in our own recent work we do not observe any activation effects for catalysts prepared from chlorine-free precursors. Consequently, we now suspect that our earlier reports [4,5] of activities which increased with time-on-stream could have been affected by unsuspected contamination by chlorine from the sample of Pd nitrate used in the catalyst preparation. Such an eventuality has been foreseen by Simone et al. [14]. We think it is possible that some, if not all, of the corresponding reports in the literature of activity

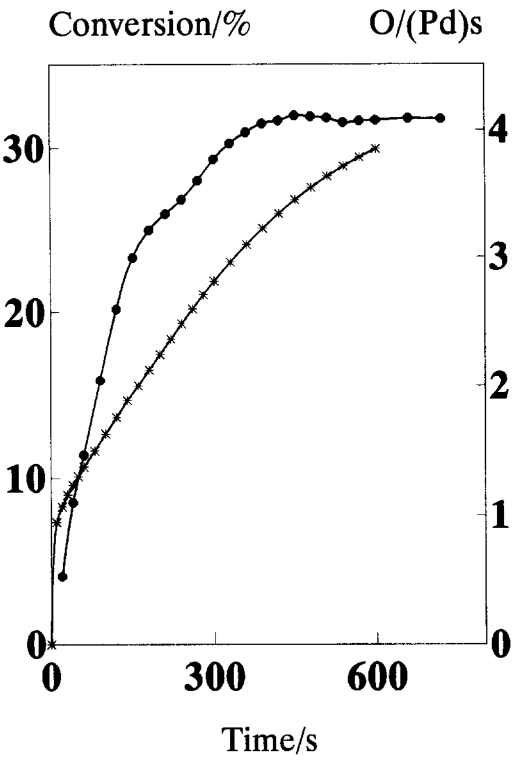


Fig. 1. Activity for methane combustion (●) and uptake of oxygen (*) by a Pd/Al_2O_3 catalyst at 300°C.

increases may have a similar explanation, especially since the absolute rate of methane oxidation in the 'active' form of the various catalysts is comparable to the activity of a 'normal' catalyst prepared from a chlorine-free precursor. This is not to claim that there are no morphological effects but to caution that there may be other explanations for some of the more dramatic effects reported in the recent literature.

To address the question of what is the optimum state of PdO_x – (Pd metal plus chemisorbed oxygen; PdO skin on a Pd metal core; bulk PdO) – we have performed some simple kinetic experiments which provide a rather clear answer to these questions. [15–18] Fig. 1 shows the rate of oxygen uptake by a prereduced $4\%Pd/Al_2O_3$ catalyst at 300°C as a function of time, and the corresponding change in the activity for the combustion of methane at the same temperature. A chemisorbed monolayer of oxygen is formed very rapidly on Pd. However, it is clear that the activity for methane oxidation is low at this stage. Clearly, at this temperature, Pd metal plus chemisorbed oxygen is not very active. Fig. 1 shows that further exposure to oxygen leads to the progressive oxidation of the Pd until the equivalent of 4 monolayers of oxygen have been taken up. For this catalyst this corresponds to essentially complete oxidation to form bulk PdO, and the formation of PdO has been confirmed in equivalent catalysts by X-ray diffraction using an in situ high temperature cell. During this progressive oxidation, the catalytic activity increases to reach a plateau when the Pd has taken up about the equivalent of 3 monolayers of oxygen. Importantly there is no further increase (or decrease) in the activity of the catalyst with time on stream (the experiment was continued for a further 40 min). These results show that the highest activity is found when the PdO is almost completely oxidised and, moreover, the activity does not decrease when bulk PdO is finally formed. It seems clear that the optimum state of PdO_x is simply a surface which corresponds to fully oxidised bulk PdO. This is equivalent to a 'skin' of PdO on Pd, but this intermediate state has no greater activity than one in which the Pd particles are fully oxidised.

Having established that bulk PdO is probably the most active state for methane oxidation does not provide a complete understanding of these catalysts because the stability of PdO is related to the oxygen partial pressure, the temperature, the support, and the previous history of the samples [6,9,14]. For example, there is a large hysteresis in the Pd/PdO equilibrium [6,8,9] and this seems to be partly due to the kinetics of reoxidation at elevated temperatures. Salomonsson et al. [19] have recently analysed these hysteresis effects in terms of a more fundamental property of the pressure–composition–temperature diagram of the three phase system: gas phase oxygen and the two solid phases, Pd and PdO_x. They anticipate that the size and location of the hysteresis loop should depend on particle size and support effects. Farrauto et al. [8] have

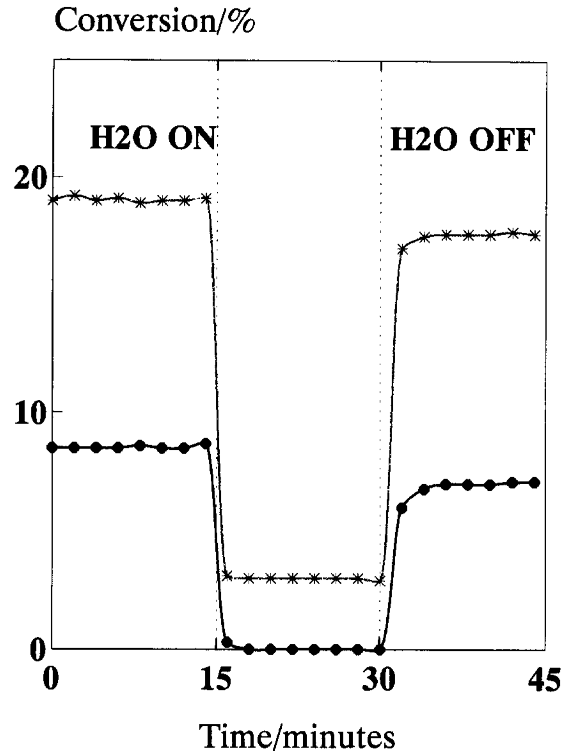


Fig. 2. Effect of water on the combustion of methane by a Pd/Al_2O_3 catalyst at 275°C (●) and 300°C (*).

indeed reported marked differences in the hysteresis effect for PdO/Al_2O_3 catalysts modified with other oxides (ZrO_2, CeO_2, TiO_2, Ta_2O_3).

As a consequence of this hysteresis it is possible to observe quite different activities for Pd catalysts when used under different operating conditions, or after different thermal pretreatments. Therefore, it is not always possible to know whether support effects or particle size effects, for example, are true primary effects or simply a secondary effect in which they influence the stability/formation of the same active phase (bulk PdO). At this stage it seems more likely that particle size effects (that is for PdO particles) and support effects have only a very minor influence on the activity of the catalyst.

A further complicating factor in comparing supported Pd catalysts for methane combustion is the inhibiting effect of the products of the reaction (CO_2 and H_2O). Ribeiro et al. [20] have reported that both CO_2 and H_2O strongly inhibit the reaction. Burch and co-workers [15] have extended this work and shown that in the presence of H_2O the effect of CO_2 is small. However, especially at lower temperatures H_2O is a severe poison. Fig. 2 shows some typical results where H_2O was introduced to a Pd catalyst at steady state. At lower temperatures the reaction is almost completely inhibited but, as pointed out by Ribeiro et al., the effect is reversible. These results can be interpreted in terms of a reversible equilibrium:

$$PdO + H_2O = Pd(OH)_2$$

where PdO represents an active state and $Pd(OH)_2$ an inactive state for methane oxidation. On this basis we have concluded that there could be circumstances, especially at lower temperatures, where the rate determining step may not be activation of the first C–H bond in methane. An alternative is that the true rate determining step is the loss of H_2O from $Pd(OH)_2$. To test this hypothesis we have performed [18] pulse experiments in which very small pulses of a 1%CH_4/air mixture were passed over 5%Pd/SiO_2 catalyst samples held in a flow of air. In a carefully dried air atmosphere at 300°C the catalyst has a very high and stable activity. (The activity is much higher than the steady state activity at this temperature.) At lower temperatures (e.g. 250°C) the catalyst shows some deactivation as the number of pulses is increased. In 'normal' cylinder air (not specially dried) the results show that the catalyst exhibits a much lower initial activity at 250°C.

We interpret these results as evidence that under reaction conditions the surface OH groups produced either by the combustion of methane, or formed by reaction with H_2O vapour in the carrier gas stream, are not easily removed at 250°C and so the initial high activity of the catalysts for the activation of the C–H bonds in methane cannot be sustained. Clearly for a completely fresh sample of PdO the rate determining step will be the breaking of the first C–H bond in CH_4. However, as soon as this happens the surface of the catalyst is partially converted into a surface hydroxide which is not active for methane oxidation. Consequently, until this surface hydroxide decomposes to release H_2O the active site is blocked and the rate of CH_4 combustion slows down. Since the desorption of H_2O is an integral part of the whole catalytic cycle, it seems that on these catalysts the true rate determining step is not C–H bond activation but O–H bond decomposition on the catalyst surface.

A further consequence of these H_2O effects is that the measured rate of CH_4 oxidation will be a function of the H_2O content of the gas stream, the temperature, and the choice of support. It is to be expected that supports with a greater affinity for H_2O would initially show higher activity since the support can scavenge H_2O and this has been proposed already by Ribeiro et al. [20] However, it is also possible that such supports, especially if they are porous, could sustain a higher local concentration of H_2O above PdO particles and result in a lower activity at steady state. This seems to be the case because we have found that whereas alumina-supported PdO (high affinity for H_2O) is more active initially than silica-supported PdO (low affinity for H_2O), at steady state the relative activities cross over.

Finally, the curious experimental fact that on PdO catalysts CH_4 is more reactive than C_2H_6 on a per molecule basis can be rationalised on the grounds that each CH_4 molecule only contributes 4 OH, whereas each C_2H_6 contributes 6 OH. If regeneration of the active site by loss of surface OH is rate determining then CH_4 would be expected to react faster as observed. However, under pulse conditions with fresh dry PdO the reverse should be the case since the C–H bonds in C_2H_6 are more reactive than those in CH_4. This is found to be the case [18] with the ratio of steady state conversions being: $CH_4{:}C_2H_6 = 1.8$, and under pulse conditions being only: $CH_4{:}C_2H_6 = 0.8$.

In summary, catalytic combustion of CH_4 on Pd catalysts appears to occur most effectively on fully oxidised PdO. Support, morphological, and particle size effects may be rather unimportant when other factors which influence the activity are excluded. These include poisoning by chlorine, inhibition by water, the effect of the support on the steady state concentration of water, and interactions of PdO with the support. The highest activity will be achieved when free PdO is present. However, this creates a problem since it is commonly the case that the most stable catalysts are those in which there is a strong interaction between the active phase and the support, so that sintering at high temperatures is minimised. In the case of supported PdO catalysts a strong interaction leads to deactivation of the catalyst by chemical effects which can more than balance any anticipated retention of activity through reduced sintering. It is not obvious that these problems can be overcome in a practical way so it seems likely that catalytic combustion will continue to require chemically quite different materials for low and high temperature operation. Whether enhanced activity at low temperatures, which is a desirable target for gas turbine operation, is feasible must also be somewhat doubtful given the serious inhibition caused by H_2O at lower temperatures. The solution might appear to be to use hydrophobic supports but how stable such a support would be in a strongly oxidising environment is another matter.

3. NO_x reduction by hydrocarbons under lean-burn conditions

The Introduction has considered briefly the opportunities for developing an acceptable ‘clean-up’ strategy for the elimination of NO_x emissions using hydrocarbons for selective reduction. Several systems have been proposed and many excellent review articles have been published recently [21,22] so it is unnecessary to repeat this information in detail at this juncture. Suffice it to note that a remarkable range of materials have been found to provide reasonable activity and selectivity for the conversion of NO_x into N_2 using a wide range of organic reductants in the presence of a large excess of oxygen. Indeed, in many cases the oxygen is mandatory. In the absence of oxygen many of these catalysts are either inactive or have only a very low activity. However, none of the systems developed so far are entirely satisfactory. For example, the zeolite-based systems have limited thermal and hydrothermal stability and are readily poisoned by H_2O (compare the effects with PdO described earlier) and SO_2. Non-redox systems tend to have low activities and are also susceptible to poisoning. Moreover, apart from the platinum group metal catalysts the reduction reaction only occurs at moderately high temperatures which is a further disadvantage. Finally, none of the catalysts exhibit high selectivity in the oxidation of the hydrocarbon (i.e., oxidation by NO in preference to oxidation by O_2). Consequently, with current catalysts it would be necessary to have quite high concentrations of organic reductant to obtain acceptable NO_x conversion.

With platinum group metal catalysts there is the potential to develop acceptable catalysts since these are already used in conventional three-way catalysts and are known to have good thermal and hydrothermal stability and resistance to poisoning. However, while they operate at low temperatures (typically 200–300°C), which is a benefit, there is an unfortunate side effect at these low temperatures which is that a significant amount (sometimes the majority) of the NO_x is converted to N_2O rather than N_2. N_2O, once formed, is not readily decomposed at these temperatures. In order to find a scientific solution to this problem it is necessary to have a good understanding of the mechanism of the selective NO_x reduction reaction on platinum-based catalysts and this is the subject of the remainder of this paper.

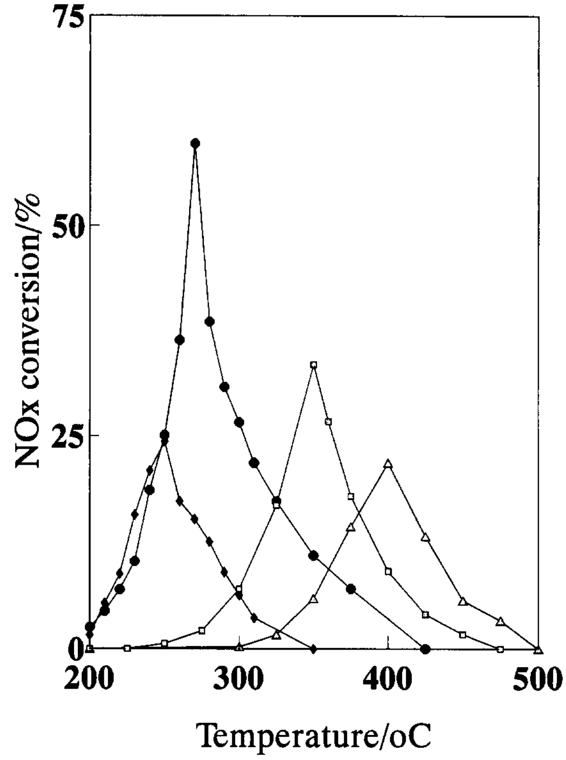
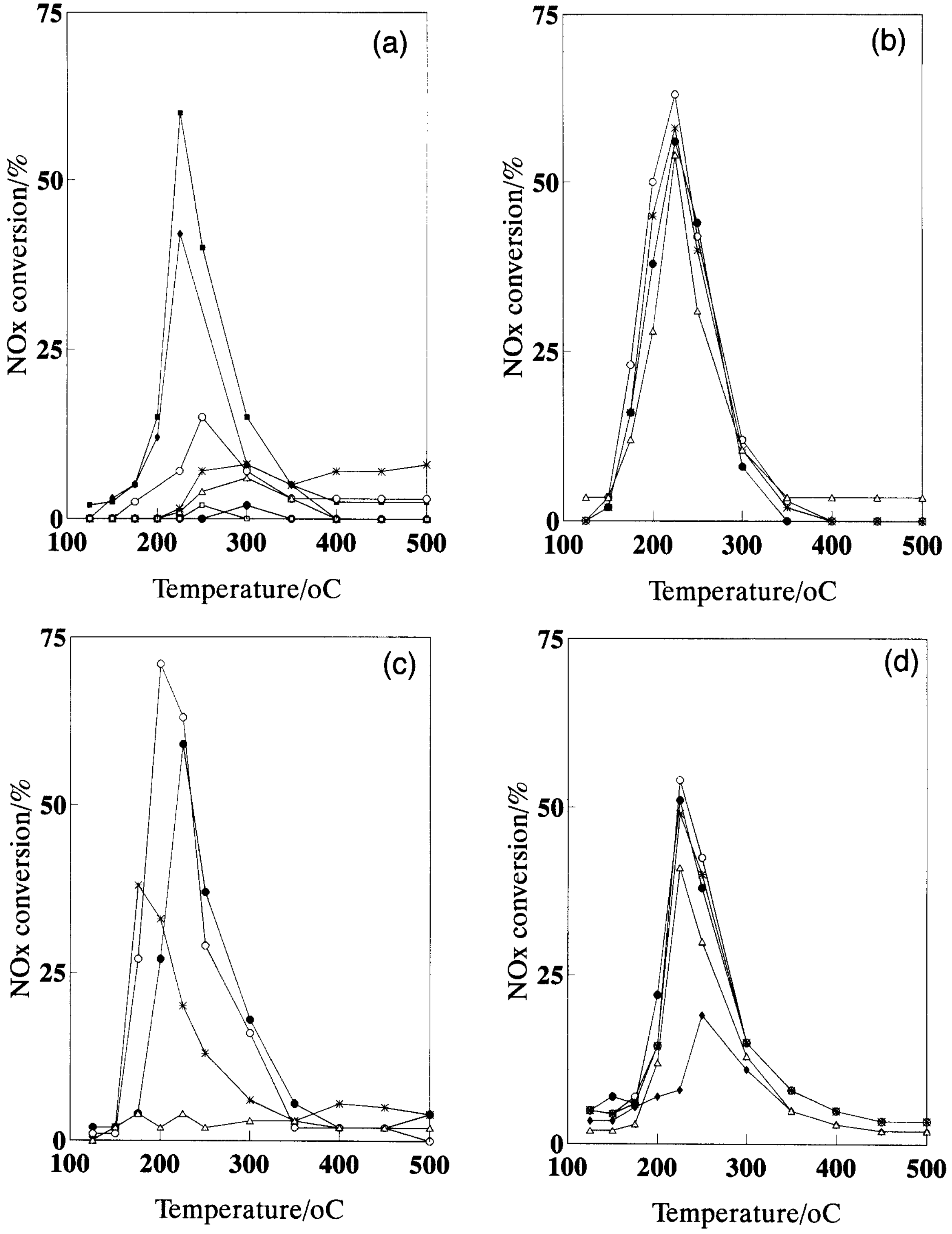


Fig. 3. NO_x conversion as a function of temperature on alumina-supported 1% platinum group metal catalysts: (●) Pt; (◆) Pd; (□) Rh; (△) Ir.

A comparison of the selective reduction of NO_x by hydrocarbons on Platinum Group metals [23] is reproduced in Fig. 3. This shows that Pt is by far the most active in the temperature range 200–300°C and so we shall concentrate attention on supported Pt catalysts. Typical results for a Pt catalyst tested with a wide range of different organic compounds is shown in Fig. 4, taken from the work of Engler et al. [24]. These results show that linear saturated hydrocarbons are only effective at higher carbon numbers, but branched chain isomers are much

Fig. 4. NO_x conversion on a Pt catalyst using various organic reductants. (a) Paraffinic hydrocarbons: (□) methane, (*) ethane, (●) propane, (△) *n*-butane, (◆) *n*-heptane, (O) isooctane, (■) *n*-hexadecane. (b) Olefinic hydrocarbons: (△) ethene, (*) propene, (O) 1-butene, (●) 1-octene. (c) Alcoholic compounds: (△) methanol, (*) ethanol, (O) 1-propanol, (●) 1-butanol. (d) Aromatic compounds: (△) toluene, (*) 1,2-xylene, (O) 1,3-xylene, (●) 1,4-xylene, (◆) 1-methylnaphthalene.


(a)
(b)
(c)
(d)
NOx conversion/%
Temperature/oC
0
25
50
75
100
200
300
400
500

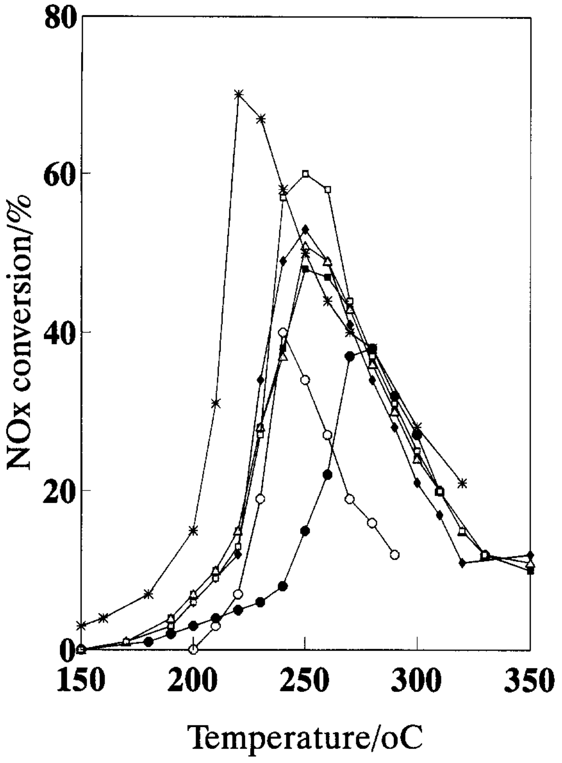


Fig. 5. NO_x reduction as a function of temperature on different metal oxide-supported Pt catalysts: (□) Al_2O_3, (*) SiO_2, (△) ZrO_2, (●) TiO_2, (■) SnO_2, (♦) WO_3, (O) MgO.

less selective at equivalent carbon numbers. Olefinic compounds are much more effective than the corresponding paraffins. Alcohols, with the exception of methanol, are very effective reductants, and aromatic compounds exhibit a moderate activity. In all cases, there is a close correlation between the rate of oxidation of the hydrocarbon and the rate of NO_x reduction. The conversion of NO_x invariably goes through a maximum which is associated with the temperature at which the hydrocarbon becomes fully oxidised. Above this temperature the Pt catalyst is effective at producing NO_2.

Support effects in the reduction of NO_x with propene can be quite significant as shown in Fig. 5, where SiO_2 is seen to be the best support and TiO_2 the worst. Pt particle size effects in the range 2.7–25 nm tend to indicate that the turnover number is significantly higher on the larger particles.

A number of mechanisms have been proposed for this reaction on platinum group metals. Zhang et al. [25] suggest that an important role of oxygen is to activate the hydrocarbon and that the selective reduction of NO proceeds via NO_2 through a reaction with the oxygen-activated hydrocarbon. Obuchi et al. [26] propose a reaction between NO_x and a partially oxidised hydrocarbon intermediate, which may be a carbonaceous radical. Sasaki et al. [27] suggest a similar mechanism in which the partial oxidation of the hydrocarbon is followed by reaction with NO or NO_2:

$$C_3H_8 + O^* = (C_pH_qO_r) \tag{1}$$

$$(C_pH_qO_r) + NO\,(\text{or}\,NO_2) = N_2 + CO + H_2O \tag{2}$$

$$(C_pH_qO_r) + O^* = CO_x + H_2O \tag{3}$$

Engler et al. [24] propose the following sequence of elementary steps:

$$NO + [S_1] = NO - [S_1] \tag{4}$$

$$NO - [S_1] + \tfrac{1}{2}O_2 = NO_2 - [S_1] \tag{5}$$

$$NO_2[S_1] = NO_2 + [S_1] \tag{6}$$

$$C_xH_y + zO_2 + [S_2] = C_xH_yO_{2z} - [S_2] \tag{7}$$

$$NO_2 - [S_1] + C_xH_yO_{2z} - [S_2] = \tfrac{1}{2}N_2O + xCO_2 + yH_2O + [S_1] + [S_2] \tag{8}$$

$$NO - [S_1] + C_xH_yO_{2z} - [S_2] = \tfrac{1}{2}N_2 + xCO_2 + yH_2O + [S_1] + [S_2] \tag{9}$$

On the other hand, Bamwenda et al. [28], on the basis of an FTIR study which detects adsorbed isocyanate species (–NCO), propose a different mechanism:

$$-NCO + O_2 = NO + CO_2 \tag{10}$$

$$= NO_2 + CO \tag{11}$$

$$2 - NCO + O_2 = N_2 + 2CO_2 \tag{12}$$

$$-NCO + [O] = NO + CO \tag{13}$$

$$-NCO + NO = N_2 + CO_2 \tag{14}$$

$$= N_2O + CO \tag{15}$$

$$= N_2 + CO + [O] \tag{16}$$

$$2 - NCO = N_2 + 2CO \tag{17}$$

In our own work we have taken a different approach [29–31] and, based on a detailed transient kinetic study, have concluded that a decomposition mechanism can explain the results for our supported Pt catalysts. At its simplest it is proposed that the organic compound removes adsorbed oxygen from the Pt surface and creates a site at which dissociative adsorption of NO can occur. Two N_{ads} combine to release N_2 into the gas phase and the O_{ads} is subsequently removed by the organic reductant.

The transient kinetic studies [29–31] demonstrate that such a mechanism is feasible but, of course, cannot prove that it is the correct mechanism, or the only mechanism, under real dynamic reaction conditions. To justify this model requires some evidence that NO decomposition, in competition with dissociative adsorption of O_2 can occur fast enough to account for the rates of N_2 formation observed experimentally. A major problem in obtaining such information comes from the fact that the Pt catalyst is self-poisoned by adsorbed oxygen so that a simple steady state NO decomposition experiment cannot be undertaken. However, by making measurements of the extent of NO decomposition at short contact times and extrapolating back to zero time it is possible to get a good estimate of the minimum rate of this reaction. Alternatively, it should be possible to use a 'non-interfering' reductant, such as H_2, to remove adsorbed O_{ads} so that the NO decomposition can continue to occur on reduced Pt sites. Table 1 compares the rate of NO decomposition at zero time with the rate of the NO/H_2 reaction and the rate of reduction of NO by propene in the presence of a large excess of oxygen.

Table 1
A comparison of the rates of NO decomposition, the NO/H_2 reaction, and the $C_3H_6/NO/O_2$ reaction on a Pt/Al_2O_3 catalyst at 240°C, after [32]

Reaction	NO turnover frequency (10^{-2} s^{-1})
$C_3H_6/NO/O_2$	0.61
NO decomposition	4.21
NO/H_2	45000

These results show that the rate of NO decomposition on a reduced Pt surface is about seven times faster than the rate of NO reduction by propene. This means that at steady state in the $C_3H_6/NO/O_2$ reaction ca. 15% of the Pt surface needs to be in a reduced state at any one time to sustain the NO decomposition reaction at the required rate. Clearly, this is possible, and so a simple decomposition mechanism seems appropriate. However, the possibility of a decomposition mechanism accounting for the observed results is further enhanced by the results for the NO/H_2 reaction on the same catalyst. Using H_2 as a reductant to remove O_{ads} we have found, as would be expected from early literature, that the rate of N_2 production is so fast that we have to measure it at temperatures below 100°C. Extrapolation to our normal reaction temperature (240°C) shows that the NO/H_2 reaction would be more than four orders of magnitude faster than the rate of N_2 formation in our lean NO_x experiments!

It is usually assumed that the NO/H_2 reaction involves NO dissociation followed by removal of O_{ads} by H_2, in which case these results clearly indicate that our decomposition model is feasible providing only that a reduced Pt site can be created. With a rate of reaction 10^4 times higher than needed, a Pt site on average only needs to be in a reduced state for a tiny fraction of the time.

Of course, H_2 is not a good reductant in the presence of O_2, but this may simply reflect the fact that the H_2 oxidation reaction is very fast and also the fact that each H_2 can only remove a single O_{ads} so that the Pt remains almost fully oxidised all the time. With propene, on the other hand, it is reasonable to argue that the reduction capacity of each molecule is such that a significant number of Pt atoms become reduced. All that is required is for a single NO molecule to reach this reduced surface before it becomes oxidised again by O_2 and if NO decomposition really is fast, the formation of N_2 can proceed very easily.

Since the decomposition of NO in the presence of H_2 is extremely fast, it seems appropriate to suggest that under dynamic reaction conditions in the $C_3H_6/NO/O_2$ reaction a similar adsorbate-assisted dissociation of NO may take place. All that may be required for this is the presence on the surface of any adsorbed species which has an affinity for oxygen. Likely candidates are H, C, CH_x (corresponding to any hydrocarbonaceous residue, not excluding oxygen-containing organic moieties), and possibly even another adsorbed nitrogen atom. As soon as an NO molecule adsorbs adjacent to such a species breaking of the N–O bond will be very rapid and the formation of N_2 can ensue.

There still remains the problem of N_2O formation in the $C_3H_6/NO/O_2$ reaction on Pt-based catalysts. From the NO decomposition model which we have proposed, the formation of N_2O is perceived to occur by the coupling of N_{ads} and NO_{ads}. Since in the presence of a large excess of O_{ads} the NO decomposition will be inhibited as compared with the rate on a fully reduced Pt surface (compare the results in Table 1), the Pt surface at steady state will contain both N_{ads} and NO_{ads}, it is difficult to see a simple way to avoid the possibility of coupling to give N_2O. Modification of the Pt surface either to further enhance the decomposition of NO or to minimise the amount of NO_{ads} may be possible. Work on such options is currently in progress.

Acknowledgements

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