Adsorbate-assisted NO decomposition in NO reduction by C_3H_6 over Pt/Al_2O_3 catalysts under lean-burn conditions

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The rates and product selectivities of the C_3H_6–NO–O_2 and NO–H_2 reactions over a Pt/Al_2O_3 catalyst, and of the straight, NO decomposition reaction over the reduced catalyst have been compared at 240°C. The rate of NO decomposition over the reduced catalyst is seven times greater than the rate of NO decomposition in the C_3H_6–NO–O_2 reaction. This is consistent with a mechanism in which NO decomposition occurs on Pt sites reduced by the hydrocarbon, provided only that at steady state in the lean NO_x reaction about 14% of the Pt sites are in the reduced form. However, the (extrapolated) rate of the NO–H_2 reaction at 240°C is about 10^4 times faster than the rate of the NO decomposition reaction thus raising the possibility that NO decomposition in the former reaction is assisted by H_{ads}. It is suggested that adsorbate-assisted NO decomposition in the C_3H_6–NO–O_2 reaction could be very important. This would mean that the proportion of reduced Pt sites required in the steady state would be extremely small. The NO decomposition and the NO–H_2 reactions produce no N_2O, unlike the C_3H_6–NO–O_2 reaction, suggesting that adsorbed NO is completely dissociated in the first two cases, but only partially dissociated in the latter case. It is possible that some of the associatively adsorbed NO present during the C_3H_6–NO–O_2 reaction may be adsorbed on oxidised Pt sites.

Keywords: lean deNO_x; mechanism; (assisted) NO decomposition; Pt/Al_2O_3

1. Introduction

The emission of NO_x from stationary and automotive sources has serious environmental implications. The three-way automotive catalyst has been highly successful in controlling exhaust emissions from conventional petrol engines which operate close to stoichiometric conditions. However, the exhaust from lean-burn engines and from diesel engines contains over 5% O_2. Under these net-oxidising conditions the three-way catalysts are no longer effective for NO_x control. To reduce NO_x under these conditions alternative catalytic systems must be developed.

The first such system to show promise was Cu ion-exchanged ZSM-5 [1–4]. However, although the Cu zeolite system has been extensively studied by many groups and has been tested in real diesel exhausts [5], it has become clear that this material is unlikely to be suitable for use as an automotive catalyst due to its thermal and hydrothermal instability. Alternative, stable, non-zeolitic materials are therefore required.

One such alternative system consists of platinum-group metals supported on metal oxides. The activity of such systems for NO_x control has recently been reported in the literature [2,6–15]. Four main mechanisms for this reaction have been proposed: (i) the oxidation of NO to NO_2 which then reacts with the hydrocarbon [7–9]; (ii) the formation of an oxidised hydrocarbon intermediate [10,11]; (iii) reduction of the metal surface followed by NO decomposition on the reduced surface [12]; (iv) the formation of an isocyanate surface species as an intermediate [13]. Combinations of these mechanisms have also been suggested, such as the oxidation of NO to NO_2 which then reacts with an oxidised hydrocarbon intermediate [14,15].

A temporal analysis of products (TAP) study of the mechanism of the deNO_x reaction over Pt/Al_2O_3 was carried out by Burch et al. [12]. Using CO, H_2 or C_3H_6 as a reductant they demonstrated that the predominant mechanism for the selective NO reduction involves the decomposition of NO on reduced Pt sites, followed by the regeneration of the active Pt sites by the reductant. In the decomposition step oxygen from the NO is retained on the Pt surface, blocking the surface from further adsorption/reaction of NO. C_3H_6, unlike CO and H_2 was found to be effective for NO reduction in the presence of O_2.

It is crucial for this "decomposition–reduction" mechanism that the rate of NO decomposition on the reduced Pt sites is rapid, otherwise the Pt will be reoxidised by the O_2 (present in excess) before the NO has a chance to decompose. In this paper the rate of NO decomposition has been investigated and compared with the rate of the lean deNO_x reaction with C_3H_6 as the reductant to see if NO decomposition is fast enough to be consistent with the proposed mechanism. The rate of NO decomposition cannot be measured under steady state conditions as the reaction only occurs over reduced Pt sites which are poisoned by the O from the NO which is retained on the Pt surface [12], i.e.

$$NO_g + Pt \rightarrow \tfrac{1}{2}N_{2,g} + Pt{-}O \qquad (1)$$

The NO decomposition has therefore been studied in two ways: (i) as the initial (maximum) rate when NO is passed over prereduced Pt catalyst and (ii) as the steady state rate of the NO–H_2 reaction, in which H_2 acts to constantly reduce the surface.

2. Experimental

The platinum on γ-alumina catalyst used in this study was prepared by incipient wetness impregnation using dinitrodiammine–Pt as the precursor. The sample was calcined at 500°C for 14 h and had a 1 wt% Pt loading, a dispersion of 69% (by H_2 chemisorption) and a grain size of 250–850 μm.

Catalytic testing was carried out using a quartz tubular downflow reactor. The sample was held between plugs of quartz wool. Reactant gases were fed from independent mass flow controllers. The reactor outflow was analysed using a Perkin Elmer Autosystem gas chromatograph with a TCD detector for O_2, N_2, CO_2, N_2O, CO, C_3H_6 and H_2O, and a Signal Series 4000 chemiluminescence NO_x analyser for NO and total NO_x (i.e. NO + NO_2). The chromatograph was equipped with a Heysep N column (80–100, s.s., 3 m × 1/8″ o.d.) for the separation of CO_2, N_2O, C_3H_6 and H_2O, and a molecular sieve 13X column (60–80, s.s., 2 m × 1/8″ o.d.) for the separation of O_2, N_2 and CO. The two columns and a 1 ml sample loop were connected to a ten-port valve. To take a sample, the valve was switched to allow the He carrier gas to flow through the sample loop, the Heysep N column, the MS column and then onto the detector. O_2, N_2 and CO pass rapidly through the Heysep N column unseparated and are subsequently separated by the MS column. The valve was then switched back, swapping the order in which the carrier gas flows through the columns so that CO_2, N_2O, C_3H_6 and H_2O pass directly to the detector after elution from the Heysep N column.

For the C_3H_6–NO–O_2 and NO–H_2 reactions, steady state measurements were made using 100 mg of catalyst in a 5 mm i.d. reactor with a feed consisting of 1000 ppm C_3H_6, 1000 ppm NO and 5% O_2 with the balance He and with a total flow of 60–300 ml min^{-1}, or 2000 ppm H_2 and 1000 ppm NO with the balance Ar and He at a total flow of 200 ml min^{-1}. Prior to the NO–H_2 reaction the catalyst was pre-treated in 20% O_2 in He for 15 min at 480°C. With the NO–H_2 reaction NH_3 analysis was achieved by mixing the reactor outflow with excess O_2 and passing the resultant mixture over a Pt/Al_2O_3 catalytic converter at 500°C. This oxidises the NH_3 to NO_x enabling the conversion of NO to NH_3 to be calculated as the difference in NO_x conversion with and without the catalytic converter, as described previously [16].

NO decomposition measurements were made using 50 mg of catalyst in a 4 mm i.d. reactor with a total gas flow of 200 or 300 ml min^{-1}. Prior to each experiment the catalyst was reduced in a flow of H_2 in Ar and He for 10 min. Increasing the reduction time to 2 h did not affect the results. The sample was then purged in He for 3–5 min and the flow switched to 1000 ppm NO in He. The reactor outflow was analysed by the GC at a known time after switching to the NO/He mix. The whole reduction and NO decomposition procedure was repeated a number of times with the GC sample being taken at different times to enable the composition of the reactor outflow to be plotted as a function of time. Switching between gas flows was achieved using two three-way solenoid valves to direct one gas flow to the reactor and the other to vent. The flow going to the vent was switched to the reactor and vice versa enabling the gas flow to be switched without causing any surge in the flow. A small N_2 background was detected in the NO/He feed and has been subtracted from the N_2 values obtained.

3. Results and discussion

The results from the C_3H_6–NO–O_2 reaction at 240°C and at a number of space velocities are given in fig. 1. At contact times below that required for 100% C_3H_6 conversion the total conversion of NO was found to be linear in contact time and the selectivities to N_2 and N_2O were independent of contact time, indicating that N_2 and N_2O are formed from a common intermediate. After 100% C_3H_6 conversion was reached, no further conversion of NO to N_2 and N_2O occurs, but NO_2 formation begins, resulting in a break of slope in the total NO conversion curve. The ratio of N_2 to N_2O formed was unaffected by 100% C_3H_6 conversion being reached. The turnover frequencies (TOF) for the consumption of NO and for NO decomposition are given in table 1. The latter was calculated assuming that the formation of one N_2 or one N_2O molecule requires the decomposition of two or one NO molecule(s), respectively, and knowing

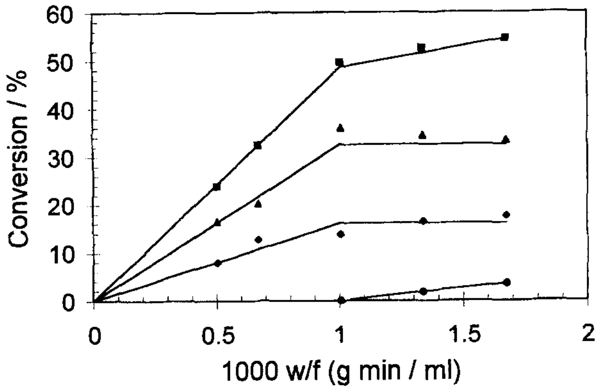

Fig. 1. The effect of varying the reciprocal space velocity, *w/f*, on the C_3H_6–NO–O_2 reaction at 240°C over 1% Pt/Al_2O_3. The breaks in slope of the lines correspond to 100% C_3H_6 conversion being reached. (Conversion of NO to N_2O (▲), N_2 (◆) and NO_2 (●) and total NO conversion (■).)

Table 1
Comparison of the C_3H_6–NO–O_2 and NO–H_2 reactions over 1% Pt/Al_2O_3 and of NO decomposition over reduced 1% Pt/Al_2O_3 at 240°C

Reaction	TOF (10^{-2} s^{-1})		Selectivity to N_2 (%)
	NO consumption[a]	NO decomposition[b]	
C_3H_6–NO–O_2	0.92	0.61	33[c]
NO decomposition	4.21	4.21	100
NO–H_2	45000[d]	45000	60[e]

[a] Rate of NO consumption per exposed Pt atom.

[b] Rate of NO decomposition per exposed Pt atom, calculated given that the decomposition of an NO molecule results in the formation of either $\frac{1}{2}N_2$, NH_3 or N_2O.

[c] Selectivity at conversions below 100% C_3H_6 conversion where N_2O is the only other N-containing product.

[d] By Arrhenius-type extrapolation from measurements at 30–65°C.

[e] NH_3 is the only other N-containing product.

that the selectivity was independent of the NO conversion, provided C_3H_6 conversion was incomplete.

Fig. 2 shows the results from the NO decomposition experiments on the reduced catalyst at 240°C for two flow rates. Zero on the time axis corresponds to the time at which the gas flow was switched from He to NO in He. There is a finite time between the point at which the switch occurs and the point at which the reaction products reach the GC, which is obviously shorter for the higher flow rate. N_2 was the only product detected. The conversion of NO to N_2 falls off rapidly with time as the reaction self poisons (see above). The TOF for NO decomposition was calculated from the initial (maximum) NO conversion. The TOFs calculated for the two flow rates were within 6% and the value given in table 1 is the average of these.

Comparison of the rates of NO decomposition over the reduced catalyst and during the C_3H_6–NO–O_2 reaction (table 1) reveals that the former is about seven times more rapid. It is reasonable for NO to decompose more rapidly on the fully reduced catalyst than in the presence of C_3H_6 and O_2, since in the latter case the Pt surface would be expected to be only partially reduced. Assuming the rate of NO decomposition over a reduced Pt site is unaffected by the presence of C_3H_6 and O_2, then this suggests that about 14% of the Pt sites are required to be in the reduced form for a simple NO decomposition mechanism to account for the rate of NO conversion (to N_2 and N_2O) in the C_3H_6–NO–O_2 reaction.

The results for the NO–H_2 reaction are given in fig. 3. This reaction occurs much more readily than either the C_3H_6–NO–O_2 reaction or the NO decomposition reaction over the reduced catalyst; reaction between NO and H_2 is detectable at 30°C and the rate of NO decomposition at 75°C is already greater than it is over the reduced catalyst at 240°C. In contrast, the reduced catalyst showed no activity for NO decomposition at 50°C in the absence of H_2. The TOF for NO consumption for the NO–H_2 reaction in the temperature interval 30–65°C is given by:

$$\mathrm{TOF}\ (\mathrm{s}^{-1}) = 9.51 \times 10^{10} \exp(-8.17 \times 10^{4}/RT)\,,$$

where R is the molar gas constant and T is the thermodynamic temperature. Extrapolation of the TOF to 240°C suggests that the rate of NO decomposition is about 10^4 times faster in the presence of H_2. At 240°C the NO–H_2 reaction produces N_2 and NH_3, but no N_2O (table 1).

The vast enhancement of the rate of NO decomposi-

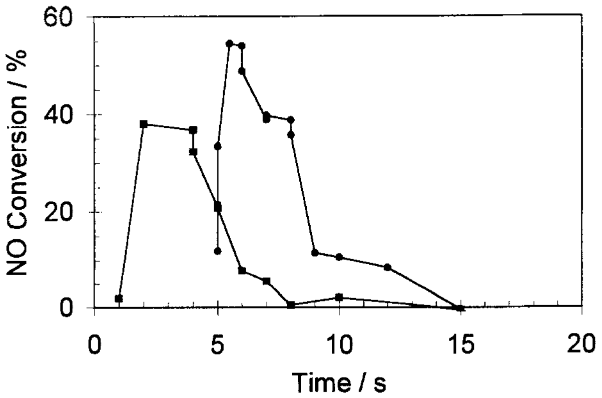

Fig. 2. NO decomposition over reduced 1% Pt/Al_2O_3 at 240°C. Time zero is time at which NO flow started. N_2 is only product. Total gas flow 200 (●) and 300 (■) ml min^{-1}.

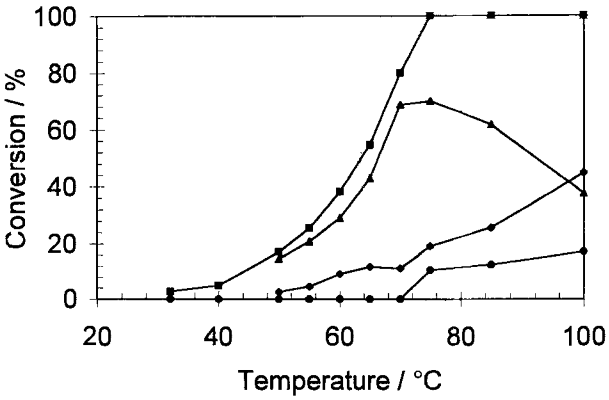

Fig. 3. The effect of temperature on the NO–H_2 reaction over 1% Pt/Al_2O_3. ((■) total NO conversion and NO conversion to N_2O (▲), N_2 (◆) and NH_3 (●).)

tion by H_2 is probably due to H-assisted NO decomposition, as first suggested by Hecker and Bell [17]. That is NO decomposition occurs by:

$$NO_{ads} + H_{ads} \rightarrow N_{ads} + OH_{ads} \quad (2)$$

rather than by:

$$NO_{ads} \rightarrow N_{ads} + O_{ads} \quad (3)$$

Calculations show that the activation energy is lower for the assisted decomposition [18]. Thus, H-assisted NO decomposition would be expected to be more rapid than unassisted decomposition, with H_{ads} acting simply to remove the O_{ads}. The occurrence of H-assisted NO decomposition is in contrast to our previous TAP study of the NO–H_2 reaction [12] which showed that no direct reaction occurred between adsorbed NO and H at 400°C. This suggests that the reaction mechanism changes with temperature, presumably because at the much higher temperature desorption of H_{ads} is more rapid, preventing reaction (2) from occurring, while the rate of reaction (3) is greatly enhanced.

Assisted NO decomposition is clearly also a possibility in the C_3H_6–NO–O_2 reaction. In this case there are a number of adsorbed species which have an affinity for oxygen and which therefore may be involved, e.g. C, CO, H, N or some fragment of C_3H_6. Thus, while it is possible that the C_3H_6–NO–O_2 reaction occurs via unassisted NO decomposition, the more rapid assisted NO decomposition would mean that the amount of the Pt surface which would need to be in the reduced form is very much less than the 14% deduced above for simple NO dissociation. This may mean that the competition between oxygen (in vast excess) and NO for the reduced Pt sites is rather unimportant.

One possible assisted NO decomposition reaction suggested in the literature is the formation of N_2 via an $[N\text{---}N\text{---}O]_{ads}$ intermediate formed from NO_{ads} and N_{ads} [17–19]. This can be regarded as an N-assisted NO decomposition,

$$NO_{ads} + N_{ads} \rightarrow [N\text{---}N\text{---}O]_{ads} \rightarrow N_{2,g} + O_{ads} \quad (4)$$

The intermediate can also desorb as N_2O:

$$NO_{ads} + N_{ads} \rightarrow [N\text{---}N\text{---}O]_{ads} \rightarrow N_2O_g \quad (5)$$

Note that while the decomposition of N_2O to N_2 has been proposed for some NO reductions [20], there are a number of reports that Pt is a poor N_2O decomposition catalyst when hydrocarbons are used as a reductant [9,21,22]. Thus, in this case further reaction of N_2O seems unlikely and hence the $[N\text{---}N\text{---}O]_{ads}$ intermediate should be regarded as a species distinct from N_2O_{ads}. This is consistent with selectivity to N_2 and N_2O being independent of contact time for the C_3H_6–NO–O_2 reaction because if decomposition of N_2O occurred, then increasing the contact time would result in increased readsorption and decomposition of N_2O to N_2 and an increased selectivity to N_2.

N_2 may also be formed by recombination of N_{ads}:

$$N_{ads} + N_{ads} \rightarrow N_{2,g} \quad (6)$$

Reactions (4) and (5), to form N_2 and N_2O, are calculated to have a lower activation energy than reaction (6) [18]. Thus reactions (4) and (5), to form N_2O and N_2, are expected to be favoured when undissociated NO is present on the catalyst. Note that N_2O is seen as a product in the C_3H_6–NO–O_2 reaction, but not with NO decomposition on reduced Pt or in the NO–H_2 reaction at 240°C. This could indicate that NO is completely dissociated at this temperature on the Pt surface in the latter two reactions preventing reactions (4) and (5) from occurring. Clearly, adsorbed associated NO is present on the catalyst during the C_3H_6–NO–O_2 reaction. It is possible that at least some of this NO is adsorbed on oxidised Pt sites, which are not present during the other two reactions; TPD experiments show that NO adsorbs without dissociation on oxidised Pt/Al_2O_3 [12]. N_2O and N_2 formation may then occur at the interface between oxidised and reduced Pt sites with an N atom on the reduced Pt combining with an NO on a neighbouring oxidised site. If this is the case then, unless the catalyst surface is completely reduced, undissociated, adsorbed NO will always be present and hence N_2O formation will always be possible. This could explain why Pt-based catalysts are prone to producing relatively large amounts of undesired N_2O. The fact that only small islands of reduced Pt are believed to be present during the C_3H_6–NO–O_2 reaction may also retard NO decomposition relative to a fully reduced surface.

The decomposition of NO in the C_3H_6–NO–O_2 reaction may be enhanced by any of the species present on the surface originating from (partially) decomposed or oxidised C_3H_6. For example, H_{ads} may be present allowing reaction (2) to occur. Other possibilities are:

$$NO_{ads} + C_{ads} \rightarrow N_{ads} + CO_{ads} \quad (7)$$

$$NO_{ads} + CO_{ads} \rightarrow N_{ads} + CO_{2,g} \quad (8)$$

$$NO_{ads} + C_xH_y \rightarrow N_{ads} + C_xH_yO_{ads} \quad (9)$$

where C_xH_y is some fragment derived from C_3H_6. Reaction (7) may go via NCO_{ads} or CNO_{ads} as intermediates. There is evidence for reaction (8) being involved in the NO–CO reaction [19,23,24]. Note that reactions (2) and (7)–(9) result in the breaking of the N–O bond without poisoning a Pt site with oxygen. Evidence that this may be occurring as a secondary, less important, mechanism comes from TAP experiments [12] which show that the maximum amount of NO which can be reduced to N_2 over Pt/Al_2O_3 is greater with a C_3H_6–O_2 mix as the reductant than with CO or H_2.

4. Conclusions

The rate of NO decomposition over reduced Pt is sufficiently fast for the lean deNO$_x$ reaction to be explained by the "decomposition–reduction" mechanism previously proposed [12], provided only that, for the conditions used here, about 14% of the Pt atoms on the catalyst surface are in the reduced form. However, it is perhaps even more likely from the present results that NO decomposition in the lean deNO$_x$ reaction is assisted by the presence of other adsorbed species, such as H_{ads}, C_{ads}, CO_{ads} and $C_xH_{y,ads}$. The relative rates of unassisted NO decomposition and H-assisted NO decomposition are in the ratio of about $10^4 : 1$. If this adsorbate-assisted NO decomposition is occurring then the proportion of Pt required to be in the reduced form at steady state is extremely small (ca. 0.01% of a monolayer).

It seems that the production of N_2O in the C_3H_6–NO–O_2 reaction over Pt catalysts can only be prevented if all the NO adsorbed on the catalyst is completely dissociated. This is unlikely as NO can only adsorb associatively on the oxidised Pt sites which are believed to be present at steady state in this reaction.

In summary, these experiments seem to demonstrate that simple NO decomposition can account completely for the rate of NO reduction in the lean NO$_x$ reaction on Pt catalysts. However, an adsorbate-assisted NO dissociation process may play an important role.

On the other hand, there does not seem to be any need to invoke the formation of specific surface intermediates (organonitro compounds, isocyanates, etc.) to account for the conversion of NO on these catalysts.

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