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The difference between alkanes and alkenes in the reduction of NO by hydrocarbons over Pt catalysts under lean-burn conditions

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The activities of Pt/SiO_2 and Pt/Al_2O_3 samples with comparable Pt dispersions for the reduction of NO_X under lean-burn conditions using C_3H_8 and C_3H_6 as the reductant is reported. C_3H_6 is more effective than C_3H_8 at reducing NO_X with both catalysts. With C_3H_6, Pt/SiO_2 exhibits greater deNO_X activity than Pt/Al_2O_3, while with C_3H_8 the opposite was observed. Kinetics measurements show that at steady state during the C_3H_6–NO–O_2 reaction the surface is dominated by carbonaceous species, while during the C_3H_8–NO–O_2 reaction adsorbed oxygen is the main surface species. As a consequence, the surface of the catalyst is quite different for the two reactions (reduced versus oxidised) and this provides a rational explanation for apparent discrepancies in the reaction mechanisms which have been proposed.

Keywords: lean deNO_X, mechanism, C_3H_8, C_3H_6, Pt/Al_2O_3, Pt/SiO_2

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.

One such alternative system consists of platinum-group metals supported on metal oxides. The activity of such systems for NO_X control has been reported in the literature [1–11]. Four main mechanisms for this reaction have been proposed: (i) the oxidation of NO to NO_2 which then reacts with the hydrocarbon [1–3]; (ii) the formation of an oxidised hydrocarbon intermediate [4,5]; (iii) reduction of the metal surface followed by NO dissociation on the reduced surface [6], possibly with the NO dissociation being assisted by other adsorbed species [7]; (iv) the formation of an isocyanate surface species as an intermediate [8]. 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 [9,10].

Recently, it has been suggested that the reaction occurs partially on the metal surface and partially on the support; Hamada et al. [11] have reported that the C_3H_8–NO–O_2 reaction occurs over Pt/Al_2O_3 and physical mixtures of Pt/SiO_2 and Al_2O_3, but not over Pt/SiO_2 alone. They suggest that the reaction occurs by a co-operative effect between Pt and Al_2O_3 either due to "spillover, gas phase transfer of reaction intermediates, or homogeneous C_3H_8 oxidation".

A possibility which does not seem to have been considered in the literature is that the mechanism may be *different* depending on the reductant used. This paper compares the activity of Pt/Al_2O_3 and Pt/SiO_2 when an alkane (C_3H_8) and an alkene (C_3H_6) are used as the reductant to examine the effect of the support and the influence of the nature of the hydrocarbon on the deNO_X activity. In addition, the effect of varying the reactant concentration has been examined to give qualitative information on the surface coverages under reaction conditions.

2. Experimental

The supported platinum catalysts used in this study were prepared by incipient wetness impregnation using dinitrodiammine–Pt as the precursor. The supports used, calcination conditions and dispersions of the final catalyst are detailed in table 1. Dispersions were determined by H_2 chemisorption. All samples had a 1 wt% Pt loading and a grain size of 250–850 μm. Samples are denoted as Pt/S(D), where S is the support and D is the percentage Pt dispersion.

Catalyst testing was carried out using a quartz tubular downflow reactor (i.d. 5 mm). The sample (100 mg) was held between plugs of quartz wool. Reactant gases were fed from independent mass flow controllers. The total flow was 200 cm^3 min^{-1}. The reactor outflow was analysed using a Perkin Elmer Autosystem gas chromatograph with a TCD detector, a Signal series 2000 IR CO_2 analyser and a Signal series 4000 chemiluminescence NO_X analyser (for NO and total NO_X (i.e.

Table 1
Catalyst preparation and characterisation. Dispersions were determined by H_2 chemisorption. All samples contain 1 wt% Pt

Sample	Support	Calcination	Dispersion (%)
Pt/SiO_2(35)	SiO_2 (Grace 432)	18 h at 500°C	35
Pt/Al_2O_3(41)	Al_2O_3 (CK300, Akzo)	18 h at 500°C	41
Pt/Al_2O_3(69)	Al_2O_3 (CK300, Akzo)	14 h at 500°C	69

NO + NO_2)). The chromatograph used a Heysep N column for the separation of CO_2, N_2O, C_3H_6, C_3H_8 and H_2O, and a molecular sieve 13X column for the separation of O_2, N_2 and CO, as described in more detail elsewhere [7]. No reaction was observed over quartz wool, provided the temperature was below 600°C.

For experiments in which the temperature was varied, the temperature was increased stepwise with constant feed composition and total flow. To determine the effect of reactant concentration, the concentration of one reactant was varied while the concentration of the other reactants was kept constant. The concentration was varied in a random way rather than sequentially, to avoid any bias in the data, e.g. due to catalyst deactivation.

3. Results

The effect of temperature on the C_3H_6–NO–O_2 reaction over Pt/SiO_2(35) is given in fig. 1. Conversion of C_3H_6 and of NO to N_2 and N_2O (i.e. NO_X conversion) both start at the same temperature, and increase with increasing temperature until 100% C_3H_6 conversion is reached. Maximum NO_X conversion occurs at this point. As the temperature is increased further the NO_X conversion decreases and conversion of NO to NO_2 begins. The conversion of NO to NO_2 increases, goes through a maximum and then decreases with increasing temperature. Similar trends were observed for the same reaction over Pt/Al_2O_3(41) (fig. 2). However, the Pt/Al_2O_3(41) was less active than the Pt/SiO_2(35) (i.e. the maximum NO_X conversion was lower and occurred at a higher temperature), despite these samples having comparable dispersions; with Pt/SiO_2(35) the maximum NO_X conversion was 69% occurring at 220°C, while Pt/Al_2O_3(41) gave a maximum NO_X conversion of 58% at 250°C.

Fig. 3 shows the effect of temperature on the C_3H_8–NO–O_2 reaction over Pt/SiO_2(35). The results are clearly very different from those obtained when C_3H_6 was used as the reductant. The hydrocarbon light-off occurs at a higher temperature and is much less dramatic compared with that obtained with the alkene. Conversion of NO to NO_2 begins at a lower temperature and occurs well before 100% hydrocarbon conversion is reached. The maximum NO_X conversion is not coincident with 100% hydrocarbon conversion being reached. The maximum NO_X conversion (5%, occurring at 250°C) was very much smaller than obtained using C_3H_6 as the reductant over the same catalyst. Similar trends were observed for the same reaction over Pt/Al_2O_3(41) (fig. 4). The maximum NO_X conversion (10%, occurring at 350–390°C) was greater than that obtained with Pt/SiO_2(35) using C_3H_8 as the reductant, but still was much less than when C_3H_6 was used as the reductant with either catalyst. C_3H_8 oxidation occurred more readily over Pt/SiO_2(35) with the temperature for 50% C_3H_8 conversion being 365 and 405°C for Pt/SiO_2(35) and Pt/Al_2O_3(41), respectively.

The effect of O_2 concentration on the rates of hydrocarbon consumption in the C_3H_6–NO–O_2 and C_3H_8–NO–O_2 reactions over Pt/Al_2O_3(69) are shown in fig. 5.

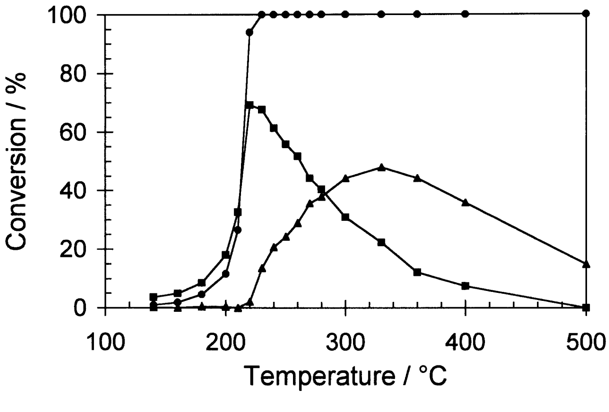

Fig. 1. The effect of temperature on the C_3H_6–NO–O_2 reaction over Pt/SiO_2(35). Reactant feed: 1000 ppm C_3H_6, 500 ppm NO, 5% O_2. (Conversion of (●) C_3H_6, (■) NO to N_2 and N_2O, (▲) NO to NO_2.)

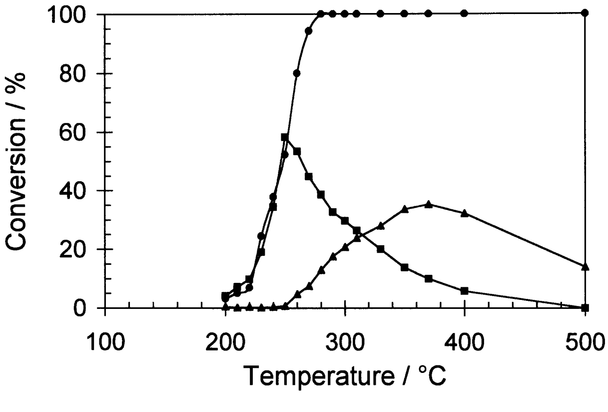

Fig. 2. The effect of temperature on the C_3H_6–NO–O_2 reaction over Pt/Al_2O_3(41). Reactant feed: 1000 ppm C_3H_6, 500 ppm NO, 5% O_2. (Conversion of (●) C_3H_6, (■) NO to N_2 and N_2O, (▲) NO to NO_2.)

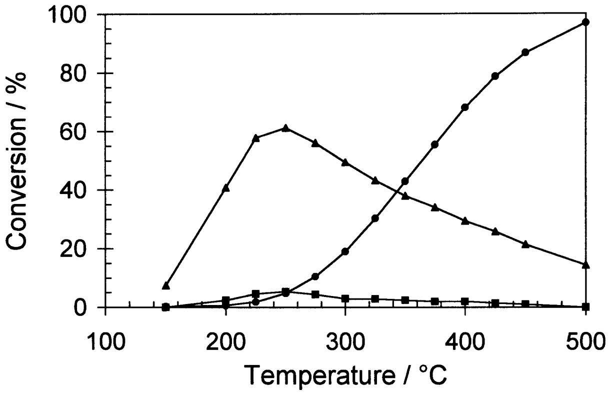

Fig. 3. The effect of temperature on the C_3H_8–NO–O_2 reaction over Pt/SiO_2(35). Reactant feed: 1000 ppm C_3H_8, 500 ppm NO, 5% O_2. (Conversion of (●) C_3H_8, (■) NO to N_2 and N_2O, (▲) NO to NO_2.)

With C_3H_6 the rate of reaction increases strongly with O_2 concentration, the rate of C_3H_6 consumption being 1.8 order in O_2. For comparison, the order in O_2 for C_3H_6 oxidation over Pt/Al_2O_3 has been reported to be as high as 2.2 [12]. The high order in O_2 suggests that the oxygen coverage on the Pt surface is very small. In contrast, with C_3H_8 the hydrocarbon oxidation is initially inhibited by O_2 and then becomes zero order in O_2 at higher O_2 concentrations. This indicates that the oxygen coverage of the Pt surface is high; as the O_2 concentration is increased, the oxygen coverage increases, blocking sites for C_3H_8 and inhibiting the reaction. When a saturation coverage of oxygen is reached, further increase in the gas phase O_2 concentration has no influence on the surface concentration of oxygen and hence the reaction becomes independent of O_2 concentration. This implies that there are still vacant sites available for C_3H_8 to react when the surface is saturated with oxygen. This is reasonable, since, for example, CO can adsorb on an oxygen saturated Pt surface [13].

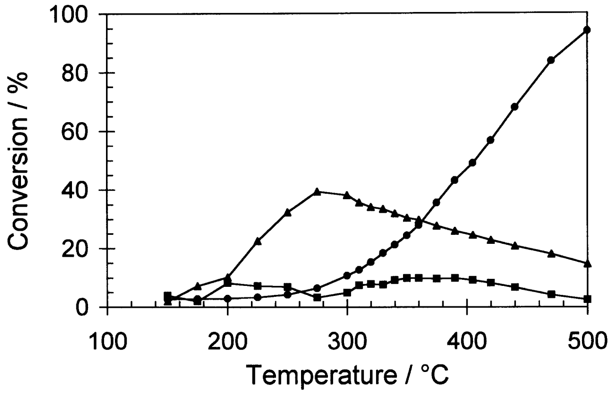

Fig. 4. The effect of temperature on the C_3H_8–NO–O_2 reaction over Pt/Al_2O_3(41). Reactant feed: 1000 ppm C_3H_8, 500 ppm NO, 5% O_2. (Conversion of (●) C_3H_8, (■) NO to N_2 and N_2O, (▲) NO to NO_2.)

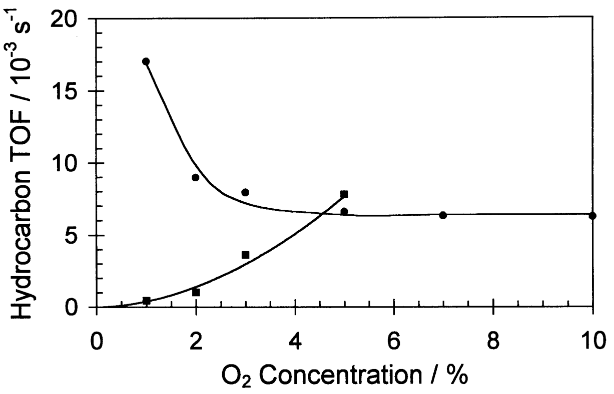

Fig. 5. The effect of O_2 concentration on the hydrocarbon TOF for the C_3H_6–NO–O_2 reaction at 240°C (■) and the C_3H_8–NO–O_2 reaction at 310°C (●) over Pt/Al_2O_3(69) with 1000 ppm hydrocarbon and 1000 ppm NO.

Fig. 6 shows the effect of hydrocarbon concentration on the rate of hydrocarbon consumption in the C_3H_6–NO–O_2 and C_3H_8–NO–O_2 reactions over Pt/Al_2O_3(69). With the C_3H_6–NO–O_2 reaction, the C_3H_6 consumption is zero order in C_3H_6, suggesting that the C_3H_6 surface coverage (or at least that of C_3H_6-derived species) is at saturation. The high coverage of these species does not seem to have an inhibiting effect on the C_3H_6 oxidation reaction possibly because C_3H_6 adsorption occurs on different sites to oxygen or because oxygen reacts directly from the gas phase. The exact opposite behaviour was observed with C_3H_8; C_3H_8 consumption is first order in C_3H_8, suggesting that C_3H_8 is either weakly adsorbed on the catalyst or reacts from the gas phase.

4. Discussion

It has been shown that Pt/Al_2O_3 and Pt/SiO_2 are both active, to some extent at least, for the reduction of NO_X under conditions of excess O_2 when C_3H_8 is used as the

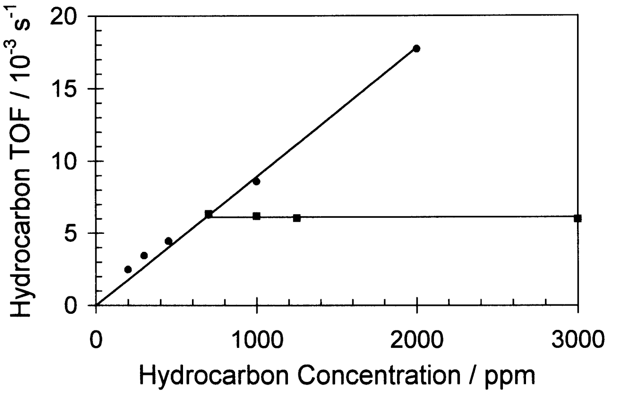

Fig. 6. The effect of hydrocarbon concentration on the hydrocarbon TOF for the C_3H_6–NO–O_2 reaction at 240°C (■) and the C_3H_8–NO–O_2 reaction at 310°C (●) over Pt/Al_2O_3(69) with 1000 ppm NO and 5% O_2.

reductant. This differs somewhat from the recent report by Hamada et al. [11], which states that Pt/Al_2O_3, but not Pt/SiO_2 is active for this reaction. They also report that physical mixtures of Pt/SiO_2 and Al_2O_3 are active and conclude that the reaction occurs by a co-operative effect between Pt and Al_2O_3. A possible explanation for these results is that the $deNO_X$ reaction with C_3H_8 occurs by two pathways, one involving Pt and Al_2O_3 and the other Pt alone, hence Pt/Al_2O_3 is more active than Pt/SiO_2, since with Pt/SiO_2 only the latter pathway would be possible. The reason for the detectable, albeit low, $deNO_X$ activity of Pt/SiO_2 in this work and the inactivity of Pt/SiO_2 reported by Hamada may be due to differences in reaction conditions, SiO_2 source, Pt precursor, Pt dispersion etc. When C_3H_6 was used as the reductant, Pt/SiO_2 was more active for $deNO_X$ than Pt/Al_2O_3, suggesting that in this case the reaction probably occurs only on the metal, with the support influencing the activity only by modifying the properties of the metal.

The kinetics results show that the state of the Pt under reaction conditions is different depending on the reductant used. When C_3H_6 is the reductant the surface is predominantly covered with C_3H_6 or species derived from C_3H_6. On the other hand, when C_3H_8 is used adsorbed oxygen is the predominant surface species. The difference in the reaction of NO to form NO_2 with the two different reductants is consistent with this model. Oxidation of NO to NO_2 presumably requires oxygen to be available on the catalyst surface. With C_3H_6, the oxygen coverage is negligible provided the C_3H_6 conversion is below 100%, hence NO_2 is only detected at temperatures above that required for 100% C_3H_6 conversion. In contrast, when C_3H_8 is used the oxygen coverage is high and hence NO_2 formation is observed even in the presence of the hydrocarbon.

The difference in dominant surface species present reflects the nature of the reductant. The double bond of C_3H_6 enables it to interact/react strongly with the Pt surface resulting in a high coverage of C_3H_6 species. C_3H_8, on the other hand, is a saturated molecule and therefore must break a bond to chemisorb on the Pt surface. The first-order kinetics of C_3H_8 oxidation suggest that the rate determining step is the dissociative adsorption of C_3H_8, from the gas phase, onto the Pt surface. The resultant adsorbed propyl species presumably reacts rapidly, resulting in no significant surface coverage on the surface, since any build up of these species would result in the order of reaction in C_3H_8 being less than unity.

Another difference in the reaction of the two hydrocarbons, is that in the C_3H_6–NO–O_2 reaction the $deNO_X$ and hydrocarbon oxidation reactions appear to be linked, while with the C_3H_8–NO–O_2 reactions this does not appear to be the case. In the C_3H_6–NO–O_2 reaction, the conversion of the hydrocarbon to CO_2 and of NO to N_2 and N_2O both start at the same temperature and increase together with temperature, until maximum NO_X conversion and complete hydrocarbon conversion are reached. In addition, Pt/SiO_2 is more active for both C_3H_6 oxidation and $deNO_X$ compared with Pt/Al_2O_3. A possible explanation for this is that, at temperatures below the onset of C_3H_6 oxidation, the surface is covered with carbonaceous species, which prevent NO from adsorbing on the surface and reacting to form N_2 and N_2O. Oxidation of these carbonaceous species results in the formation of vacant sites onto which NO can adsorb and react. As the temperature is increased, the C_3H_6 TOF and hence the rate at which vacant sites become available increases and hence the rate of NO_X conversion also increases. It is also possible that the $deNO_X$ reaction may occur via NO dissociation which is assisted by an intermediate of the hydrocarbon oxidation [7].

In the case of the C_3H_8–NO–O_2 reaction, the maximum NO_X conversion is not linked to the attainment of 100% hydrocarbon conversion. Moreover, while Pt/SiO_2 is better than Pt/Al_2O_3 at oxidising the hydrocarbon, Pt/Al_2O_3 is better at NO reduction. It is interesting to note that during the C_3H_8–NO–O_2 reaction, the surface is covered predominately with oxygen, which is what the state of the Pt surface is likely to be after 100% hydrocarbon conversion is reached in the C_3H_6–NO–O_2 reaction. It is also at this point that the NO_X conversion in the latter reaction begins to fall off. Thus it may be concluded that a high oxygen coverage of the surface is not favourable for the reduction of NO by hydrocarbons. It is also notable that the C_3H_6 will not react with NO in the absence of O_2 over Pt/Al_2O_3 (presumably because surface sites are blocked by carbonaceous species – see above), while higher NO_X conversions are possible with C_3H_8 in the absence of O_2 [14], suggesting that O_2 and NO compete to react with C_3H_8.

5. Conclusions

We propose that the main differences between the results obtained by Hamada and co-workers for the $\mathbf{C_3H_8}$–NO–O_2 reaction and by Burch et al. for the $\mathbf{C_3H_6}$–NO–O_2 reaction are due to the fact that the state of the catalyst in each case is different. In one case (C_3H_6–NO–O_2) the Pt is reduced and covered with carbonaceous species. In the other (C_3H_8–NO–O_2) the catalyst is oxidised and covered with adsorbed oxygen. It is not surprising that Pt and PtO might have different catalytic properties and it is equally not surprising if two different mechanisms for NO reduction should apply. For a reduced (Pt) surface, NO decomposition can explain the results, whereas for an oxidised (PtO) surface, the bifunctional mechanism proposed by Hamada and co-workers could explain the results observed, especially the difference between Pt/SiO_2 and Pt/Al_2O_3 noted in their work.

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