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# **Beneficial and problematic interactions between NO<sub>x</sub> trapping materials and carbonaceous particulate matter.**

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## **Abstract**

The presence of a NO<sub>x</sub> trapping BaO component with a Pt active phase does not *per-se* promote carbon combustion. However when coupled with trap regeneration promotion of soot combustion is seen. Operating NO<sub>x</sub> trapping materials promote combustion due to the periodic localised increases in [NO<sub>2</sub>]<sub>(g)</sub> generated during the regeneration rather than due to a co-generated exotherm. However, it has been noted that the presence of soot prevents NO<sub>x</sub> traps from employing their full trapping capacity.

*Keywords:* Particulate combustion, NO<sub>x</sub> trap promotion, transient studies.

## **Introduction**

Carbonaceous Particulate Matter (PM) forms around sulphur nucleation sites within combustion chambers of diesel engines and has several well documented adverse affects both on human health and the urban and global environment [1-3]. One method for the removal of such particulates from exhaust streams involves trapping them within cordierite monolith filters and subsequently oxidising them to CO<sub>2</sub> [4]. During this process either O<sub>2</sub> or NO/O<sub>2</sub> mixtures can be used as oxidants [5]. The presence of NO improves the rate of combustion and the mechanism of this promotion involves the transfer of an oxygen atom to soot particles *via* an NO<sub>2(g)</sub> intermediate [6], Scheme 1.

Another after-treatment system used in the purification of diesel or lean-burn gasoline engines is a NO<sub>x</sub> trap. This removes NO from a fuel-lean exhaust stream by converting NO<sub>(g)</sub> into Ba(NO<sub>3</sub>)<sub>2(s)</sub> through reaction with O<sub>2</sub> and BaO. The first step in this conversion is the oxidation of NO into NO<sub>2</sub>, *i.e.* the same step that operates in the NO promotion of soot combustion detailed above. Once the trap becomes saturated it is regenerated by a pulse of hydrocarbons and the NO<sub>x</sub> released and reduced on a Rh

component [7]. A simplified scheme of NO<sub>x</sub> storage and reduction is shown in Scheme 2.

The combination of these two features in the after-treatment system of a diesel engine would be a major advancement in the development of 4-way catalysts [8-10], *i.e.* a single bed catalysing the removal of CO, Volatile Organic Compounds (VOC), NO<sub>x</sub> and PM from the exhaust of fuel efficient diesel vehicles (the Toyota DPNR concept).

There have been relatively few reports [11-14] of materials that can both store NO<sub>x</sub> for and NSR cycle and also combust soot using an NO<sub>2</sub> promoter. This is unusual given that the same first step operates in both cycles and materials that have activity in one cycle might be expected to show some activity in the second. Significantly, there have been recent reports [11, 15, 16, 18] that the combustion of PM from diesel exhausts can be improved through the incorporation of a NO<sub>x</sub> trapping component within the filter.

Also there are relatively few reports regarding any detrimental interactions between NO<sub>x</sub> traps and soot combustion catalysts although Makkee *et al.* [14] have reported that the NO<sub>x</sub> storage capacity of NSR materials decreases upon aging under soot oxidising conditions.

In this work we have evaluated the effect of the presence of a NO<sub>x</sub> trapping component (BaO) upon the activity of model 0.3% Pt/SiO<sub>2</sub> catalysts for promoting the combustion of soot. We also analyse for any effects that the presence of soot has upon the behaviour of the NO<sub>x</sub> trap in terms of NO<sub>x</sub> trapping capacity.

## **Experimental**

### *Catalyst Preparation*

The model catalysts studied, 0.3% Pt/SiO<sub>2</sub> and 0.3%Pt/5%Ba/SiO<sub>2</sub>, were prepared using standard wet impregnation techniques from solutions of H<sub>2</sub>Pt(OH)<sub>6</sub> (dissolved in dilute HNO<sub>3</sub>) and Ba(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub> dissolved in water. The SiO<sub>2</sub> was provided by Grace and had a surface area of 256 m<sup>2</sup>g<sup>-1</sup>. SiO<sub>2</sub> rather than the more conventional Al<sub>2</sub>O<sub>3</sub> was chosen as a support due to the fact that it does not interact with or store NO<sub>x</sub> and this makes de-convolution of the transient experiments (see later) more straightforward.

Accurately weighed samples of  $\text{H}_2\text{Pt}(\text{OH})_6$  sufficient to yield a nominal Pt loading of 0.3% were dissolved in ~1ml (sufficient to fill the pores of the support material) of 0.5M  $\text{HNO}_3$  and the solution was added dropwise to 1g of  $\text{SiO}_2$ . The mixture was then dried overnight at 110 °C and calcined in air for 2h at 500 °C.

Similarly accurately weighed samples of  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ , sufficient to yield a Ba loading of 5% Ba, were dissolved in 1 ml of water and the solution was again added dropwise to 1g of  $\text{SiO}_2$ . This mixture was then dried and calcined as before.

In the ternary catalyst ( $\text{Pt/Ba/SiO}_2$ ) the  $\text{SiO}_2$  was firstly impregnated with Ba, dried and calcined before subsequently being impregnated with Pt (again followed by drying and calcination steps) in order to maximise the exposure of the Pt which is the active component in the  $\text{NO} \rightarrow \text{NO}_2$  transformation.

#### *Activity Measurements*

Activity in the soot combustion reaction was studied by holding the catalyst/soot mixtures (Degussa Printex L) with quartz wool in a reactor tube connected to a gas manifold and an online GC (Shimadzu FID GC 8A fitted with a methanator) or mass spectrometer (Prolab). The catalysts were mixed with soot in a 1 part catalyst:2 part soot ratio. A mixture of catalyst (212-350  $\mu\text{m}$ ) and soot was mixed thoroughly using a spatula (approximating a “loose contact” situation) and subsequently this mixture was wet into a paste using the minimum amount of  $\text{CH}_3\text{OH}$ . The paste was then dried (to remove methanol) and the resultant solid sieved to particle sizes of (212-350  $\mu\text{m}$ ). This treatment provides some adhesion between the catalyst particles and the carbon.

The combustion of soot in the mixtures was studied under *pseudo*-steady state conditions, *i.e.* in a flow of  $\text{O}_2$  (4%) or  $\text{O}_2$  (3.4%) and NO (1320 ppm) in  $\text{N}_2$  at several temperatures and under transient conditions, *i.e.* at 400 °C in a flow of He with periodic injection of various combinations of NO,  $\text{O}_2$  and  $\text{H}_2$  through the manipulation of electrically actuated 4-way valves. It should be noted that during the transient studies when a gas is switched into the reactant stream an equivalent volume of He is removed thus keeping the overall flow constant.

### *Temperature Programmed Desorption*

A fresh sample of Pt/Ba/SiO<sub>2</sub> was exposed (at 400 °C) to NO (1250 ppm) and O<sub>2</sub> (4.5 %) mixture for 60 s in the presence and absence of soot. In both cases the same mass of catalyst was used so direct comparison of the profiles generated is possible. The catalyst (or catalyst/soot mixture) was then cooled to 300 °C and subsequently ramped in a flow of He to 650 °C at a ramp rate of 20 °C min<sup>-1</sup>. The exit gases were continuously monitored using on line mass spectrometry.

## **Results and Discussion**

### *Pseudo steady-state reactions*

Figure 1 shows the *pseudo* steady-state activities of the Pt/SiO<sub>2</sub> and Pt/Ba/SiO<sub>2</sub> catalysts as a function of temperature in the presence and absence of NO. Obviously more combustion takes place in all cases at higher temperatures but it can also be clearly seen that over both catalysts the production of CO<sub>2</sub> is enhanced in the presence of NO due to the operation of the mechanism shown in Scheme 1.

Control experiments in the presence and absence of NO either using SiO<sub>2</sub> support material or Ba/SiO<sub>2</sub> as a catalyst show lower activities than these catalysts in the combustion in O<sub>2</sub> and there is no effect on activity seen following the addition of NO – showing the necessity of an NO oxidation functionality for promotion.

What is also noticeable is that there is no discernable difference in activity between the Pt/SiO<sub>2</sub> catalyst and the Pt/Ba/SiO<sub>2</sub> material, *i.e.* there is **no** promotional effect seen once a NO<sub>x</sub> trap is incorporated into the catalytic mixture. If anything, the presence of Ba slightly poisons the reaction when NO is in the feed. Therefore the presence of a NO<sub>x</sub> trapping component coupled with a Pt active phase does not promote steady state soot combustion. We have previously noted similar results over BaO combined with less active (regarding the promotion of the NO→NO<sub>2</sub> reaction) FeZSM-5 catalysts [17].

Suzuki *et al.* [11] have noted increased combustion of PM following the incorporation of a NO<sub>x</sub> trap into the catalytic material. However, their experiments involved transient Temperature Programmed Reaction monitoring of the production of CO<sub>2</sub>. These measurements are obviously not steady-state or *pseudo* steady-state in nature. They

ascribe this increased activity to direct contact between the soot particles and the nitrated  $\text{NO}_x$  storage material. Following the results obtained above, where nitrated  $\text{NO}_x$  storage material behaves in exactly the same manner as catalysts without such sites, we suggest rather, that Suzuki's results are due to desorption of  $\text{NO}_2$  from the  $\text{NO}_x$  storage sites as the temperature is raised and the subsequent use of this  $\text{NO}_2$  to either combust  $\text{C}_{(\text{s})}$  or activate it for combustion with  $\text{O}_2$ . Such processes cannot take place in the absence of the  $\text{NO}_x$  storage component and hence promotion is seen in the presence of  $\text{NO}_x$  traps.

### *Transient Studies*

However, it should be recalled that once operational  $\text{NO}_x$  traps do not work under steady-state or *pseudo*-steady state conditions (see Scheme 2). For 99% of the time the  $\text{NO}_x$  storage and reduction catalyst exists under a flow containing (as reactive species) mostly  $\text{O}_2$  and  $\text{NO}$  (as the flow in which the *pseudo*-steady state measurements were taken above). Once the BaO  $\text{NO}_x$  trap is saturated, it is regenerated using a rich pulse of hydrocarbons. The material exists in this mixture  $\sim 1\%$  of the time (Scheme 2). These hydrocarbons regenerate the BaO trapping material, cause the release of  $\text{NO}_{2(\text{g})}$  and reduce the Rh component of a catalyst to the metal (upon which  $\text{NO}_x$  is subsequently reduced) while concomitantly themselves oxidising to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

It has also been reported that that an alternatively lean and rich operation promotes soot oxidation to a greater extent than a constant lean atmosphere [18]. Suzuki and Matsumoto [11] ascribe this to a second mechanism of promotion (as well their "contact" mechanism discussed above) and discuss this mechanism in terms of "activated species decomposed under the rich atmosphere" oxidising PM.

There are two features of this rich pulse that could be envisaged to promote PM combustion, *i.e.* (a) the localised exotherm caused when the hydrocarbons combust and (b) the transient localised increase in  $[\text{NO}_2]_{(\text{g})}$ . In their article [11] Suzuki and Matsumoto neglected to account for the possibility of the former effect causing promotion of soot combustion.

In order to determine which of these two potentially promotional mechanisms is the more important in promoting combustion over the  $\text{NO}_x$  trapping materials we have

attempted to mimic these effects of NO<sub>x</sub> trap regeneration (exotherm and NO<sub>2</sub> increase) over a Pt/SiO<sub>2</sub>/soot mixture in a flow of NO/O<sub>2</sub> at 400 °C using pulses of different gas mixtures.

Firstly, pulses of H<sub>2</sub> (which immediately combusts at this temperature) were added to mimic the exotherm generated when hydrocarbons interact with Pt/Ba(NO<sub>3</sub>)<sub>2</sub> in the presence of O<sub>2</sub> and secondly, pulses of NO were added mimic the latter effect, *i.e.* transiently increased concentrations of [NO<sub>2</sub>]<sub>(g)</sub>. In both cases before the experiment was begun the samples were subjected to periodic treatments in O<sub>2</sub> and NO/O<sub>2</sub> in order to remove any heterogeneous carbon from the system.

Figure 2 shows the CO<sub>2</sub> profiles formed during these transient experiments. It should be noted that control experiments performed over the SiO<sub>2</sub> support materials and Ba/SiO<sub>2</sub> catalysts show that their soot combustion activities remain relatively unaffected by either pulses of H<sub>2</sub> or NO.

At the beginning of the experiment the mixture is held in a flow of He at 400 °C. After 1 minute NO (1100 ppm) and O<sub>2</sub> (4 %) are switched into the flow and soot combustion commences (as measured by on-line mass spectrometry). The system is left for a further minute and then the second gas (NO, increasing overall [NO] to 3060ppm or H<sub>2</sub>, giving a [H<sub>2</sub>]<sub>inlet</sub> of 3000 ppm) is switched in for 10 seconds. The system is then left in a flow of NO/O<sub>2</sub> for 30 seconds. This pulse sequence is repeated a further 4 times before the NO/O<sub>2</sub> is finally switched out. For clarity in figure 2 only one point in 100 is labelled to distinguish the different profiles.

Figure 2 clearly shows that the addition of extra NO<sub>x</sub> is a much more important feature in terms of promoting soot combustion than the exotherm generated when H<sub>2</sub> is combusted (measured to be of the order of 5 °C).

Interestingly when only O<sub>2</sub> is used as an oxidant the overall conversion to CO<sub>2</sub> is much lower (as expected since the promotional effect of NO is removed) but the effect of the H<sub>2</sub>-generated exotherm is proportionately much greater. This is shown as the lower profile in figure 2.

The results presented above have shown that of the two mechanisms suggested by Suzuki and Matsumoto for the NO<sub>x</sub> traps promotion of soot combustion (a) contact between a soot particle and nitrated NO<sub>x</sub> trap and (b) the activated species decomposed under the rich atmosphere oxidising soot, that the latter is of far greater importance. We have also discounted a previously unconsidered possibility, *i.e.* that the exotherm caused by regeneration is the reason for the increase seen in soot combustion activity. This does not preclude the possibility that a larger exotherm caused by the combustion of higher concentrations of hydrocarbons would have a larger effect.

#### *Effects of PM on NO<sub>x</sub> storage capacities*

Having ascertained the reason why NO<sub>x</sub> traps promote the combustion of soot the final area of interest in this work was to evaluate whether the presence of soot in any way affects the *sorption capacity* of a NO<sub>x</sub> trap. This feature directly affects the first step in the NO<sub>x</sub> trap cycle, *i.e.* where NO is oxidised to NO<sub>2</sub> over Pt and subsequently the NO<sub>2</sub> adsorbs on, and reacts with, BaO. We studied this effect using a Temperature Programmed Desorption technique to analyse the concentrations of NO<sub>x</sub> adsorbed on a fresh sample of Pt/Ba/SiO<sub>2</sub> following exposure (at 400 °C) to NO (1250 ppm) and O<sub>2</sub> (4.5 %) mixture for 60 s in the presence and absence of soot. The catalysts were then cooled to 300 °C and subsequently ramped in a flow of He to 650 °C at a ramp rate of 20 °C min<sup>-1</sup>. Control experiments studying adsorption of NO<sub>x</sub> onto (and desorption of NO<sub>x</sub> from) SiO<sub>2</sub>, Ba/SiO<sub>2</sub>, Pt/SiO<sub>2</sub> and soot alone have shown that the adsorption onto each of these species is negligible under the conditions of the experiment.

Both materials show desorptions which are characteristic of the decomposition of Ba(NO<sub>3</sub>)<sub>2</sub> [19] and, from figure 3, it is clear that the sample which had been dosed in the presence of soot desorbs (and thus initially adsorbs) far less NO<sub>x</sub> than that which was dosed in the absence of soot (643 μmol g<sup>-1</sup> as against 205 μmol g<sup>-1</sup>).

While the former concentration is relatively close to the theoretical limit for the formation of Ba(NO<sub>3</sub>)<sub>2</sub> (the loading of Ba is 364 μmol g<sup>-1</sup> giving a maximum NO<sub>x</sub> trapping capacity of 728 μmol g<sup>-1</sup>) increases in the length of the dosing time shown (60s) have little effect on the latter NO<sub>x</sub> loadings (results not shown).



As an aside, only very small amounts ( $<10\ \mu\text{mol}$ ) of CO (confirmed as CO rather than  $\text{N}_2$  by analysis of the  $m/e = 12$  signal) were formed during the TPD. Therefore the possibility that equivalent amounts of  $\text{NO}_x$  were initially adsorbed onto the Pt/Ba/ $\text{SiO}_2$  material in the presence and absence of soot but that in the presence of soot desorbing  $\text{NO}_2$  was reduced to  $\text{N}_2$  and soot concomitantly oxidised can be discounted as the reason for seeing less desorbed  $\text{NO}_x$ . Less NO desorbed from the second material simply because initially less was adsorbed during the dose.

This result shows that the presence of soot decreases the sorption capacity of the  $\text{NO}_x$  trapping component. The obvious explanation for these observations is that in the presence of soot the  $\text{NO}_2$  formed over the Pt component (a necessary prerequisite to the formation of  $\text{Ba}(\text{NO}_3)_2$ ) reacts with soot before reacting with BaO (see Scheme 3).

This feature, *i.e.* the fact that the  $\text{NO}_x$  trapping component is less able to store  $\text{NO}_x$  in the presence of soot, has consequences for the engine management cycle required to most efficiently operate a  $\text{NO}_x$  trap (regarding frequency of regeneration or catalyst  $\text{NO}_x$  trap loadings required for efficient  $\text{deNO}_x$ ) if amalgamating these two functions ( $\text{NO}_x$  removal and Particulate Matter combustion) is to be considered in so called 4-way catalysis.

There is a possible further consequence of the presence of soot on the NSR cycle which relates to the reduction step. The desorbed species in NSR ( $\text{NO}_2$ ) is reduced over a Rh component and it has been widely reported that  $\text{NO}_2$  is a more active oxidant (and thus easier to reduce) than NO [20, 21]. Therefore there is also an issue with the possibility of carbon reducing liberated  $\text{NO}_2$  to NO before the reduction component of the NSR catalyst “sees” and fully reduces it to  $\text{N}_2$ . If the particular reduction process relies on a concentration of  $\text{NO}_2$  rather than of NO (which can be the case in lean- $\text{NO}_x$  reduction with hydrocarbons [20] or  $\text{NH}_3$  [21]) then this might also decrease the effectiveness of the NSR cycle. Further work is ongoing to determine whether this is the case.

## Conclusions

We have found that the reason that BaO promotes particulate combustion is related to the transient release of  $\text{NO}_2$  during trap regeneration. The exotherm generated during

the regeneration plays a more minor role in the promotion (although it is more significant in the absence of NO). On the other hand the activity of nitrated BaO in promoting soot combustion is negligible. The presence of soot, on the other hand, is detrimental to the performance of a NO<sub>x</sub> trap since it offers another reaction route for the utilisation of NO<sub>2</sub> rather than the desired formation of Ba(NO<sub>3</sub>)<sub>2</sub>.

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Figure 1

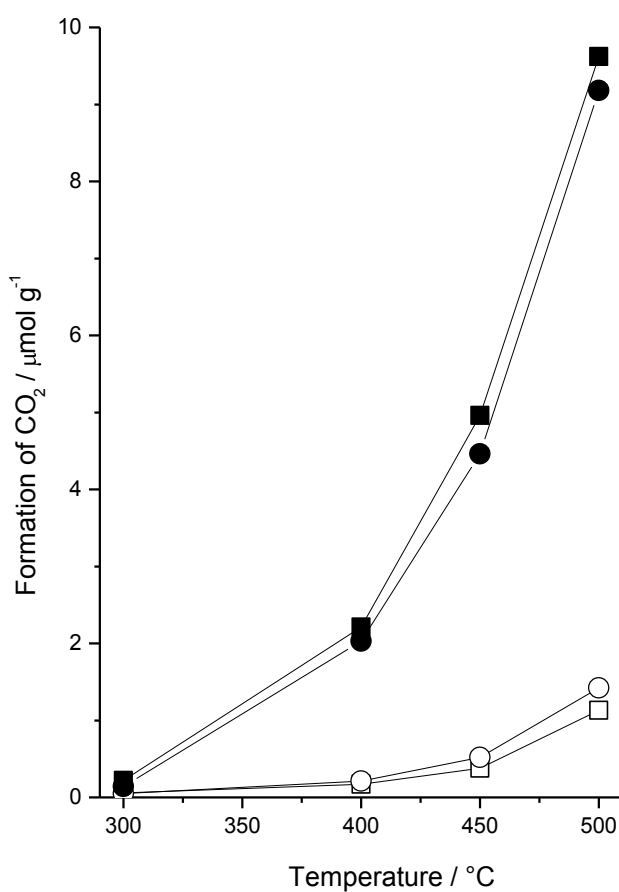


Figure 1: *Pseudo* Steady-State soot combustion activity of Pt/SiO<sub>2</sub> (□,■) and Pt/Ba/SiO<sub>2</sub> (○,●) catalysts using air (open symbols) and NO/air (filled symbols) as oxidants.

Figure 2

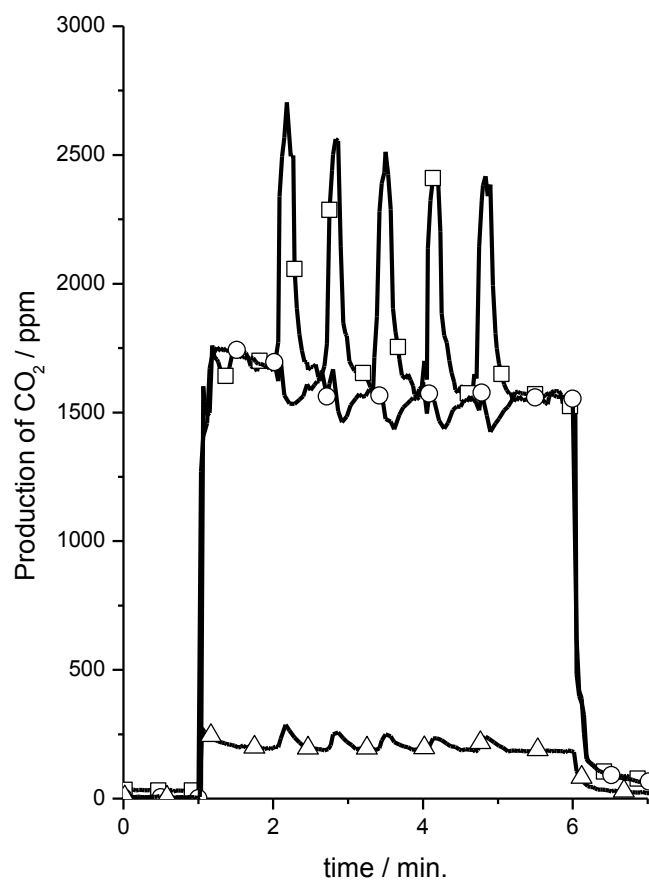


Figure 2: Transient production of CO<sub>2</sub> from a 0.3%Pt/SiO<sub>2</sub> catalyst/soot mixture in a flow of NO + O<sub>2</sub> with periodic injection of NO (□) and H<sub>2</sub> (○). The lower profile (Δ) shows the effect of injecting H<sub>2</sub> into a stream of O<sub>2</sub> over the catalyst/soot mixture.

Figure 3

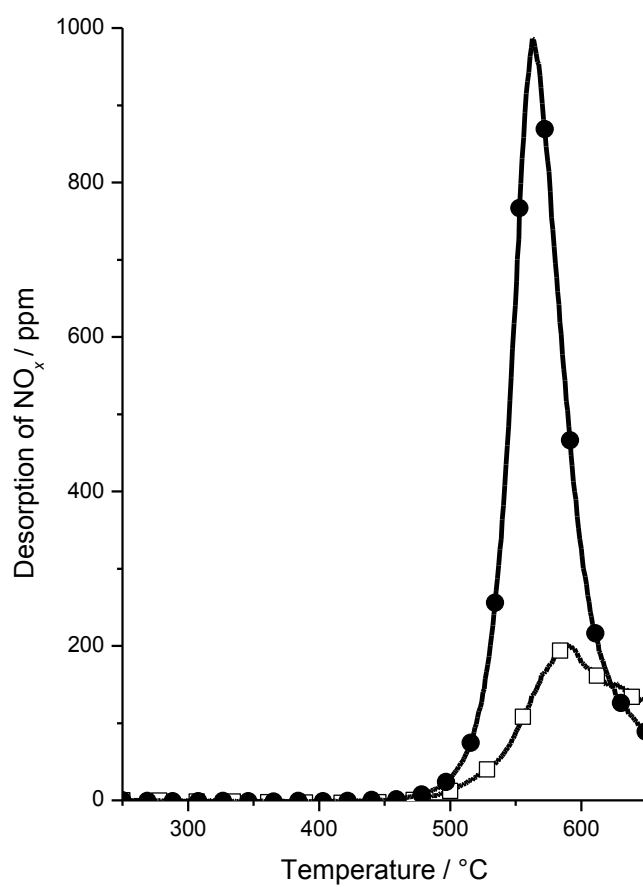
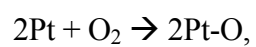
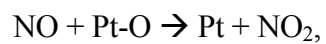


Figure 3: TPD of NO from Pt/Ba/SiO<sub>2</sub> dosed with equivalent concentrations of NO/O<sub>2</sub> at 400 °C in the presence of soot (□) and in the absence of soot (•).

### Scheme 1



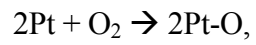
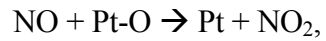
followed by



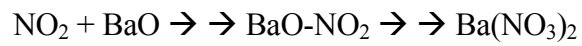
Scheme 1: A simplified mechanism showing NO promotion of soot combustion.

## Scheme 2

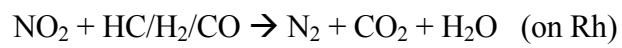
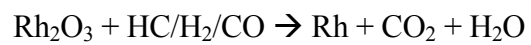
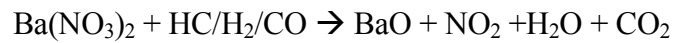
### **NO<sub>x</sub> Storage (99% of time)**



followed by

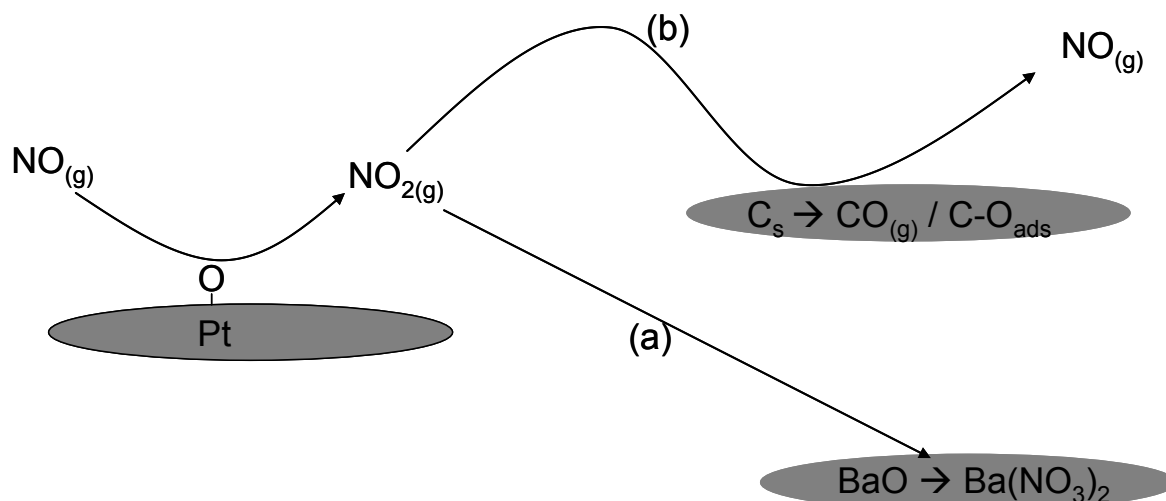


### **NO<sub>x</sub> Reduction (1% of time)**



Scheme 2: A simplified mechanism showing NO<sub>x</sub> storage and reduction

Scheme 3



Scheme 3: The proposed mechanism by which Particulate Matter decreases the  $\text{NO}_x$  adsorption capacity of a  $\text{NO}_x$  trap.  $\text{NO}_2$  formed over oxidised Pt can either adsorb on BaO (eventually forming  $\text{Ba}(\text{NO}_3)_2$ ) (route a) or, in the presence of PM, interact with carbon and become reduced to NO (route b). The latter route then precludes the formation of  $\text{Ba}(\text{NO}_3)_2$ .