A method for obtaining stable, high activity for NO_x reduction at low temperatures

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Very high and stable low temperature activity for the reduction of NO by *n*-octane on a 0.3 mass% Pt/Al_2O_3 catalyst operating under lean burn conditions may be achieved by secondary injection of micropulses of clean-burning thermal promoters into the gas stream.

Oxides of nitrogen (NO_x) formed in the combustion of diesel fuel are recognised as severe atmospheric pollutants and are the subject of increasingly stringent emissions control legislation[1,2] and so diesel engines will soon require comparable exhaust emissions technology to that used for petrol engines. However, although there has been much research on NO_x removal in fuel-lean exhaust streams,[3–6] to date no suitable material has been developed which will attain the levels of activity required under diesel operating conditions. Of the various materials examined, supported Pt catalysts appear to offer the best low temperature activity, are resistant to poisoning by SO_x, and are hydrothermally stable.[1,2,4,5] However, the goal of obtaining high activity at low temperatures, without rapid deactivation, has yet to be realised. Here, we address this problem and present preliminary data concerning the use of microinjection techniques to achieve highly active low temperature $DeNO_x$ catalysts.

The catalyst used in this study was the commercial catalyst CK303, ex Akzo (0.3 mass% Pt on Al_2O_3, pre-reaction surface area 226 m^2 g^{-1}, metal surface area 0.48 m^2 g^{-1}, Pt particle diameter 1.7 nm). It was chosen primarily as a low cost material having modest low temperature activity.[3,4] All catalyst testing was performed in a standard microreactor system described elsewhere.[3] Prior to testing, all samples were aged overnight in a standard reaction mixture (100 mg catalyst, 500 ppm NO, 500 ppm *n*-octane, 5% O_2, balance He, total flow 200 ml min^{-1}) at 500 °C and then 'cleaned' (550 °C in 5% O_2 in He for 1 h). *n*-Octane was chosen as a reductant to simulate a real fuel. NO_x conversions were determined by on-line analysis using a standard chemiluminescence detector (Signal series 4000), with samples logged onto a PC at 6 s intervals. CO_2 analysis was performed using a Signal series 2000 IR analyser. No reaction was observed in the absence of a catalyst.

The profile for the $DeNO_x$ reaction over a range of temperatures was analysed and gave results typical of those found in the literature with the conversion to N_2 rising to a maximum at *ca.* 220 °C[3,4–8] (results not shown). However we have previously shown that temperature programming studies may not be a reliable measure of catalyst activity[7] because of deactivation as the catalysts is heated up from lower temperatures. Therefore we have examined the lifetime of clean catalysts under isothermal conditions at temperatures close to the *n*-octane light-off point (*ca.* 220 °C when using CK303 as the catalyst, defined as the temperature required for $>20\%$ conversion of *n*-octane). The activity was clearly sensitive to temperature (Fig. 1). Indeed, only at 220 °C was the activity stable, whilst at lower temperatures the timescale for steady activity became increasingly small. Hence at 170 °C catalyst deactivation occurred so rapidly that reactor response lag and NO_x adsorption mask any NO_x reduction. This was reflected in the low amount of CO_2 produced, and the absence of an in-bed exotherm.[3,7] In contrast, reaction at 185 °C [steady activity for *ca.* 65 min, see Fig. 1(*c*) and Fig. 2(*a*)] was ascribed to catalytic reaction only. The decline in activity is ascribed to surface deposition of unreacted (carbonaceous) intermediates.

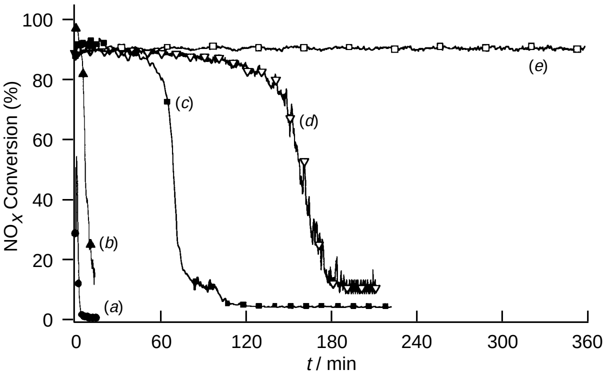

Fig. 1 Effect of temperature on the activity of CK303 (0.3 mass% Pt on Al_2O_3) under standard reaction conditions (100 mg catalyst, 500 ppm NO, 500 ppm *n*-octane, 5% O_2–He, balance He, total flow 200 ml min^{-1}). (*a*) 170 °C (●), (*b*) 180 °C (▲), (*c*) 185 °C (■), (*d*) 200 °C (▽), (*e*) 220 °C (□)

To circumvent this process of deposition leading to deactivation the method of micropulse injection was devised. This entailed injection of minute quantities of 'thermal promoters', *i.e.* readily combustible molecules, into the standard reaction mixture. It was envisioned that the combustion of these molecules would create an exotherm within the catalyst bed, and more specifically at the reaction centres. The ensuing temperature rise would promote reaction/desorption of any deposits located thereon.

The injection of small quantities of H_2 [Fig. 2(*b*)], gave no significant improvement in lifetime. However a bed exotherm of *ca.* 20 °C was recorded some 10 s after the injection, although it is clear that the temperature rise at any active site would be significantly larger, with associated desorption of surface NO_x as evidenced by the sharp (negative) peaks. However, the use of

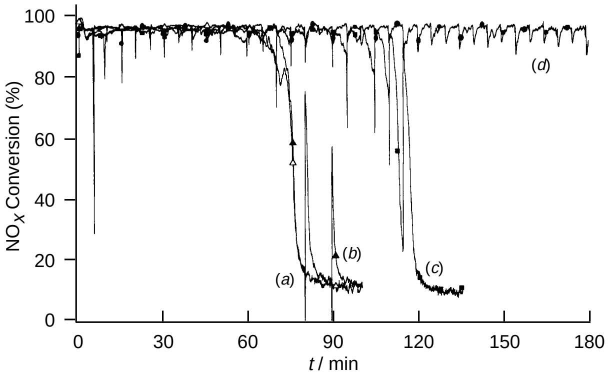

Fig. 2 Effect of microinjection on the activity of CK303 under standard reaction conditions, at 185 °C. (*a*) No injection (▽), (*b*) 0.5 ml H_2 every 10 min (▲), (*c*) 2 ml of H_2 every 5 min (■), (*d*) 1 μl of MeOH every 5 min- (●)

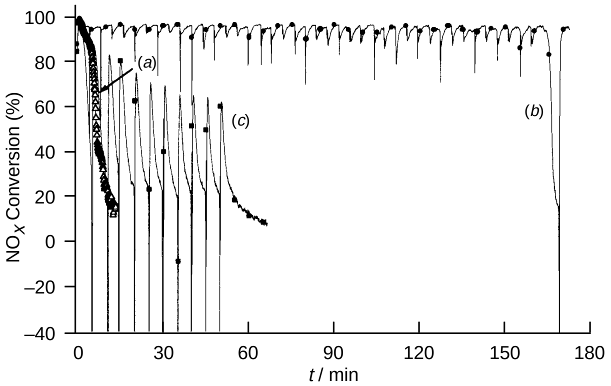

Fig. 3 Effect of microinjection on the activity of CK303 under standard reaction conditions at 180 °C. (a) No injection (▽), (b) pulse feed of 2 μl MeOH only every 4 min (■), (c) 2 μl MeOH every 4 min (●). Note after 160 min injections stopped and then recommenced at 169 min.

larger, more regular pulses of H_2 was found to be beneficial [Fig. 2(*c*)], and increased catalyst lifetime by *ca*. 30 min. This was consistent with the increased and more regular exotherm (bed temperature increase of *ca*. 30 °C) and associated desorption/reaction of NO$_x$ and other adsorbates.

The use of pulses of methanol was even more successful [Fig. 2(*d*)] with no deactivation being observed for >4 h on line (associated bed exotherm 40–45 °C). This is clearly a very significant result and suggested a means for obtaining high activity with no deactivation at low temperatures.

Given the successful application of methanol micropulsing at 185 °C its use at 180 °C was attempted. Previously, complete deactivation of CK303 had been observed in *ca*. 6 min [Fig. 3(*a*)] but by pulse injection (2 μl every 4 min, bed exotherm *ca*. 45 °C) deactivation was circumvented [Fig. 3(*b*)]. Injection was ceased after 160 min and deactivation occurred within 6 min in exactly the same manner as observed earlier with the clean catalyst [Fig. 3(*a*)]. Injection of MeOH at 169 min however, resulted in complete recovery of activity. These data confirm that the methanol effectively cleans the Pt surface to enable DeNO$_x$ to occur.

The methanol pulse itself is not the primary reductant as can be seen from the reaction of MeOH pulses in the absence of the *n*-octane feed [Fig. 3(*c*)]. In this case there is some DeNO$_x$ activity but this decreases rapidly to a low value. Thus it is clear that the very high activity obtained when MeOH is injected into a gas stream containing *n*-octane is due to the micropulsing in conjunction with the *n*-octane feed.

These results provide a novel, practical method for obtaining high activity for DeNO$_x$ reactions under diesel exhaust conditions at low temperatures.

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Notes and References

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