Particle size and support effects on the activity and deactivation of Pt-based catalysts for the reduction of NO by *n*-octane under lean-burn conditions

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Very high and stable activity for the reduction of NO by *n*-octane under lean-burn conditions may be achieved at temperatures as low as 180 °C by the use of supported Pt catalysts, providing the catalyst is clean and is comprised of large Pt particles.

The adverse environmental impact of NO_x is well known and is the subject of increasingly stringent emissions control legislation.[1,2] It is now accepted that diesel engines will soon require comparable exhaust emissions control to that used on petrol engines. However, despite intensive research into the field of lean DeNO$_x$,[3–6] no suitable material has yet been developed which will attain the levels of activity required under real operating conditions. The problems encountered range from SO$_x$ poisoning to hydrothermal instability, particularly for zeolite-based materials.[1,5] In contrast, Pt-based materials are resistant to SO$_x$ and have good hydrothermal stability.[2,4,5] However, the primary goal of obtaining stable low temperature activity has yet to be realised. Here, we address this problem and present preliminary data concerning highly active low temperature DeNO$_x$ catalysts.

The catalysts used in this study were prepared by incipient wetness impregnation using platinum dinitrodiammine precursor (ex Johnson Matthey), followed by drying (24 h, 120 °C) and calcination (12 h, 550 °C) to give nominal Pt loadings of 1%. The exception to this was the commercial catalyst Azko CK303 (0.3% Pt/Al$_2$O$_3$). All catalyst testing was performed in a standard microreactor system described elsewhere.[3] Prior to reaction all samples were aged overnight in standard reaction mixture (100 mg catalyst, 500 ppm NO, 500 ppm *n*-octane, 5% O$_2$, balance He, total flow 200 cm^3 min^{-1}) at 500 °C. Subsequently, all samples were 'cleaned', *viz.* calcined at 550 °C in 5% O$_2$ in He for 1 h. *n*-Octane was chosen as a model reductant to simulate a component in a real fuel. NO_x conversions were determined by on-line analysis using a standard chemiluminescence detector (Signal series 4000), with data 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. H$_2$ chemisorption was performed in a facility constructed in-house using conditions described elsewhere.[3] Metal particle diameters were calculated assuming a spherical geometry. BET surface areas were determined by standard N$_2$ adsorption.

Previously much importance has been placed upon the analysis of temperature profiles for DeNO$_x$ catalysts.[4–6] Moreover, such studies have been performed upon 'aged' materials to simulate exhaust catalyst lifetime performance. Conversely, in the present study it was found that profile measurements were not a reliable indication of catalyst activity. Hence isothermal activity profiles of the catalysts were determined using 'clean' samples at temperatures in the region of the hydrocarbon light off (defined as the temperature required for >20% hydrocarbon combustion, in these studies *ca*. 220 and 195 °C for 0.3% Pt/ Al$_2$O$_3$ and 1% Pt/Al$_2$O$_3$, respectively). By this method it is possible to obtain information on the activity of catalysts in the absence of any surface deposition. This premise is reflected in Fig. 1 which compares the activity of a 0.3% Pt/Al$_2$O$_3$ catalyst at 198 °C. Trace 1, in which the catalyst was temperature
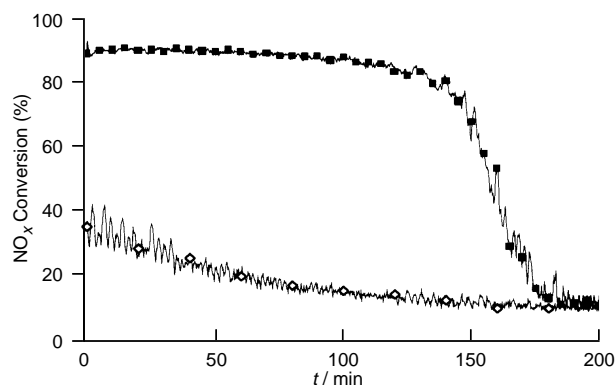

Fig. 1 Effect of surface retention upon activity of 0.3% Pt/Al$_2$O$_3$ at 198 °C. **1**, ($\diamondsuit$), DeNO$_x$ activity after exposure to reaction mixture at lower temperatures; **2**, ($\blacksquare$), DeNO$_x$ activity of 'clean' surface.

profiled from 150 °C, exhibits a severe loss of activity *cf*. trace 2 obtained for the 'clean' surface. Thus it is clear that this frequently adopted procedure for evaluating catalysts may seriously underestimate their intrinsic activity.

Fig. 2 illustrates the response of several 1% Pt catalysts under 'clean' reaction conditions. The data further demonstrate that high DeNO$_x$ activity is possible below the hydrocarbon light-off temperature. In all cases there was an initial period of high activity for NO reduction (>90% NO$_x$) and for *n*-octane combustion (100% conversion of *n*-octane to CO$_2$). The high combustion activity resulted in a marked increase in catalyst temperature (at least 30 °C, as indicated by in-bed thermocouple).

The duration of the initial period of high activity (see Fig. 2) was found to be dependent on the reaction temperature and the choice of catalyst support as summarised in Table 1. Thus, while the SiO$_2$-supported catalyst exhibited very rapid deactivation below 190 °C, the activity of 1% Pt/ZrO$_2$ was constant at temperatures as low as 180 °C for >10 h. Similarly for 1% Pt/ Al$_2$O$_3$, decreasing the furnace temperature from 180 to 175 °C halved the catalyst lifetime. In all cases the decrease in DeNO$_x$ activity was mirrored by a loss of combustion activity.

Some of these features are attributed to variable metal/ support interactions. With SiO$_2$ there is minimal support interaction and hence the catalysis occurs exclusively on unmodified metal particles. In contrast, both Al$_2$O$_3$ and ZrO$_2$ can interact with the Pt and facilitate surface reactions[7] and hence the reaction is not so constrained. Moreover chemisorption results (Table 1), indicate that both the SiO$_2$- and Al$_2$O$_3$-supported samples contain comparatively small Pt particles. Hence it appears that the combination of a non-interacting support and small Pt particles is responsible for the poor low temperature stability of the ex SiO$_2$ sample. Conversely the low temperature stability of 1% Pt/ZrO$_2$ is ascribed to the positive combination of these factors.

To test this hypothesis the 1% Pt/Al$_2$O$_3$ sample was subjected to a high temperature treatment in 5% O$_2$–He (740 °C for 24 h) to induce sintering. This increase in particle size was clearly beneficial to DeNO$_x$ activity (Fig. 3). Comparative studies of
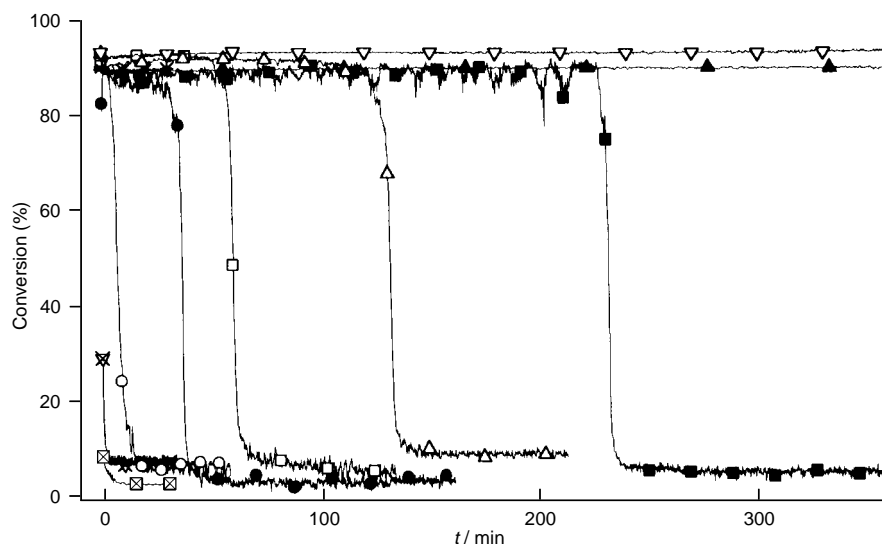
Fig. 2 Effect of the choice of the support and the temperature on the activity of supported Pt catalysts for NO reduction by *n*-octane (100 mg catalyst, 500 ppm NO, 500 ppm *n*-octane, 5% O_2–He, balance He, total gas flow rate was 200 cm³ min⁻¹). Key: (⊠), SiO_2/175 °C; (⊗), SiO_2/185 °C; (*) SiO_2/190 °C; (○), Al_2O_3/170 °C; (□) Al_2O_3/175 °C; (△), Al_2O_3/180 °C (▽), Al_2O_3/185 °C; (●), ZrO_2/170 °C; (■), ZrO_2/175 °C; (▲), ZrO_2/180 °C.

Table 1 Characterisation and catalytic performance data for the materials under investigation

Catalyst 1% Pt	Pt size[a]/ nm	MSA[a]/ m² g⁻¹	BET/ m² g⁻¹	Lifetime @ temperature (°C)/min				
				170	175	180	185	190
Al_2O_3	2.0	1.4	218	5	60	130	∞[b]	∞
SiO_2	3.5	0.8	296	—	< 1	—	1	∞
ZrO_2	11	0.26	16	40	240	∞	∞	∞
Al_2O_3[c]	12	0.24	160	15	130	∞	∞	∞

[a] Metal surface area (MSA) and Pt particle size determined from H_2 chemisorption. [b] ∞ indicates beyond the end of the experiment. [c] Sample sintered at 740 °C, in 5% O_2–He for 24 h. In all cases lifetime is defined as the period for which NO_x conversion > 80%.
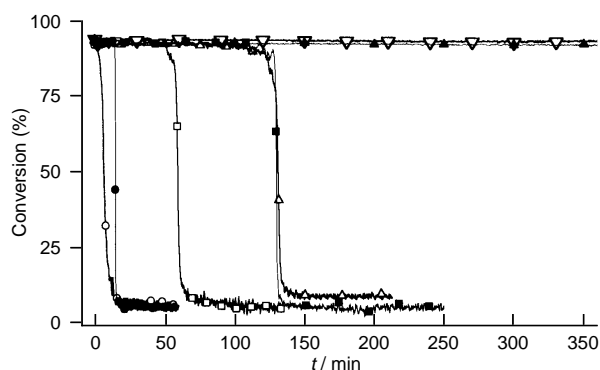

Fig. 3 Effect of sintering on the activity of 1% Pt/Al_2O_3 under standard reaction conditions. Key: (○), 170 °C; (□), 175 °C; (△), 180 °C; (▽), 185 °C; (●), sintered 170 °C; (■), sintered 175 °C; (▲), sintered 180 °C.

the original and the post-sintered samples demonstrated significant improvements in the performance at lower temperatures. The minimum operating temperature for high activity DeNO$_x$ without deactivation was lowered, and the stability of the sintered catalyst was far superior to that of the pre-sintered case with lifetimes at comparable temperatures being more than doubled.

This increased poison tolerance reflects the complex balance in these DeNO$_x$ catalysts owing to the competition for surface sites between the reductant and oxidants, as has been found previously.[8] It further reflects the adverse effects of the

retention of reaction intermediates, whether derived from organic compounds or from NO$_x$, as clearly illustrated in the differences observed in isothermal and temperature-programmed studies. Future work will address the nature of the deposits responsible for deactivation. However at this stage any attempt to identify these poisoning species would be mere speculation and outside the scope of this communication.

These preliminary results have an important technological value concerning the evaluation of the real intrinsic activity of DeNO$_x$ catalysts. Three significant points emerge. First, the intrinsic activity of clean Pt catalysts for NO reduction by higher hydrocarbons may be much higher than would be observed under normal testing conditions because of the rapid and serious deactivation observed at temperatures (*ca.* < 170 °C) below the hydrocarbon light-off region. Second, the lowest apparent activity is observed for supports, such as SiO_2, which do not strongly interact with Pt particles and so perhaps do not provide any resistance to deactivation. Third, the intrinsic activity and stability of large Pt particles is much greater than that of small Pt particles. Hence for a specific support, Pt particle size rather than metal–support interaction seems to be dominant, since the available data suggest that deactivation is initiated at the Pt:support interface. Irrespective of the origin of the enhanced performance it is clear that this information may prove useful in the development of more active catalysts for NO reduction under lean-burn conditions.

Notes and References

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