

A catalytic trap for low-temperature complete NO reduction in oxygen-rich media

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Nitric oxide is reduced to nitrogen in oxygen-rich media at temperatures as low as 250 °C over CuO/Al₂O₃ catalyst pretreated with liquid hydrocarbons.

Removal of nitrogen oxides from the exhaust of stationary and automotive sources containing large concentrations of oxygen remains a challenging problem. Noble-metal three-way catalysts operating under reductive conditions are not effective in the presence of oxygen due to the very high catalytic activity toward combustion of the reductant (hydrocarbons and carbon monoxide). Cobalt- and copper-zeolite catalysts have been shown to operate effectively in the process of NO reduction by gaseous hydrocarbons under oxidative conditions,¹⁻³ but due to the lack of stability zeolite-based catalysts do not provide a viable solution to the problem.⁴ Transition-metal oxides, which are more promising than zeolites in terms of stability, also have been extensively studied as catalysts for the selective reduction of NO under oxidative conditions.^{5,6} With small alkenes as the reductant and at temperatures in the range 400–600 °C these catalysts have shown remarkable activity in selective NO reduction. However, as has been pointed out,⁴ it is highly improbable, that for automotive sources a reductant other than those already existing on board will be used. Also, catalysts must be able to operate under temperatures close to the diesel engine exhaust temperature (below 300 °C).

Herein we report results of our study, in which we have found that NO can be completely reduced to nitrogen, in the presence of oxygen, by liquid hydrocarbons at low temperature over a metal oxide catalyst using the catalytic trap mode: *i.e.* the catalyst was treated with liquid hydrocarbon prior to reaction with gas containing NO and oxygen.

The key to this finding is the formation of stable intermediates on the catalyst surface during preliminary treatment with liquid hydrocarbons. These intermediates possess high reactivity towards NO reduction in the presence of oxygen in the reaction mixture.

Copper oxide supported on alumina was used as the catalyst (17% CuO/Al₂O₃). The NO reduction was performed by the following procedure: the catalyst was placed in the reactor and treated for a period of time with a helium flow in which a certain concentration of liquid hydrocarbon had been added, the hydrocarbon flow was then stopped and the mixture of NO and oxygen passed through the 'catalytic trap'.

A first set of experiments has been performed in pulse mode with 0.2 g of the catalyst. The catalyst was treated with 33 ppm of decane in helium at 100 °C for 10 min. The catalyst was then heated to 250 °C and pulses of a mixture, containing 1000 ppm NO and 5% O₂ in helium were passed through the trap. The single pulse volume was 0.9 ml and the flow rate 25 ml min⁻¹. The results are presented in Fig. 1.

In the first pulse the nitrogen evolution corresponded to <90% conversion. After 5 pulses the evolution of nitrogen reached about 110% of NO conversion. It can be supposed that the reason for the lower nitrogen evolution in the first pulse is the necessity to accumulate a sufficient concentration of nitrogen-containing compounds on the catalyst surface, which eventually decompose to form molecular nitrogen. In fact, the quantity of 'under-evolved' nitrogen on the left side of

maximum on the curve (Fig. 1, pulses 1–4) correspond to the 'over-evolved' nitrogen on the right side of maximum (>100%). Eventual decline of nitrogen evolution (after pulse 10, Fig. 1) is presumably related to the consumption of surface species formed in the process of hydrocarbon interaction with the catalyst surface.

A second set of experiments was performed by continuous passing of a NO–O₂ mixture through the reactor with the catalyst preliminary treated with liquid hydrocarbon (the catalytic trap mode) and the results are summarised in Table 1.

It can be seen that nitric oxide in the mixture containing 8% O₂ is completely reduced at a space velocity of 14 000 h⁻¹. Treatment of the catalyst with a leaded petrol-containing

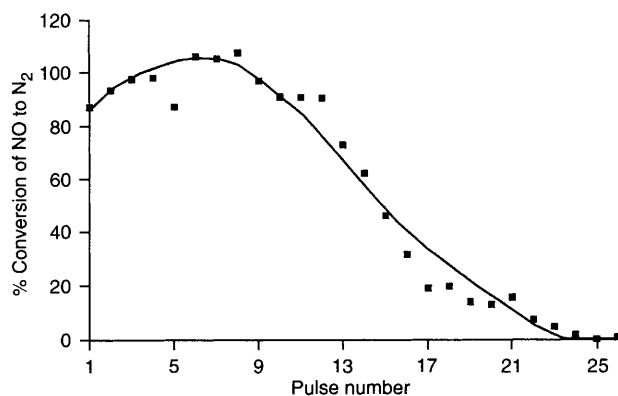


Fig. 1 NO reduction at 250 °C in pulse mode over 17% CuO/Al₂O₃ catalyst pretreated with decane (0.2 g of catalyst, pulse volume 0.9 ml, pulse composition: 1000 ppm NO, 5% O₂ in He. Catalyst pretreatment: 33 ppm of decane in He, 100 °C, 10 min).

Table 1 NO reduction by liquid hydrocarbons in the catalytic trap mode (catalyst: 17% Cu/Al₂O₃, reaction mixture: 8% O₂, 1000 ppm NO, balance He; space velocity = 14 000 h⁻¹)

Pretreatment	T ^a /°C	t ^b /s	NO conv. to N ₂ (%)
473 ppm, decane in He, 100 °C, 5 min	250	30	70
754 ppm, decane in He, 100 °C, 10 min	275	45	100
754 ppm, diesel in He, 100 °C, 10 min ^c	290	35	84
754 ppm, decane in He, 100 °C, 10 min after treatment with leaded petrol ^d	275	45	100

^a Run temperature. ^b Run time. ^c Quantity of added diesel corresponds to the quantity of decane giving a concentration of 754 ppm. ^d Before the run the catalyst was exposed to a mixture of 8% oxygen, 1000 ppm NO, 754 ppm leaded fuel, balance He, at 275 °C for 6.5 h (quantity of added fuel corresponds to the quantity of decane, giving a concentration of 754 ppm).

mixture does not affect the catalytic activity. Hence the system could potentially be used for cleaning exhaust gases of engines using a leaded fuel.

No conversion of nitric oxide into nitrogen was observed in blank experiments when the catalyst has not been preliminary treated with liquid hydrocarbons. The study of NO reduction at different temperatures revealed that at temperatures above 400 °C a decrease in NO conversion, due to coking of the catalyst, was observed.

As has been pointed out, the high activity of the catalyst towards NO reduction during the 'trap period' can be explained by the formation on the catalyst surface of stable intermediates during the 'treatment period', such intermediates being much more reactive towards NO than the hydrocarbon itself. It has been shown previously that saturated hydrocarbons react with the surface of copper oxide to form carboxylate like species^{7,8} and the formation of such species occurs at temperature as low as 100 °C.⁸ The reactivity of these species must be much higher than that of the hydrocarbon itself (C–C and C–H bonds of the carboxylate complexes are much weaker than those of hydrocarbons). As these species are formed on the regular oxygen sites of the surface, their concentration on the surface will be very high. Even at very low partial pressures of hydrocarbon complete coverage of the catalyst surface can be achieved.⁸ This is also beneficial for NO reduction as one can suppose that at least two nitrogen-containing surface species are located nearby to each other to enable formation of an N₂ molecule.

Thus, NO can be reduced by liquid hydrocarbons (including diesel fuel) in the catalytic trap mode in the presence of high

concentrations of oxygen at temperatures as low as 250 °C and space velocities above 10000 h⁻¹ during the reduction step. The treatment time is still quite high. Even taking into account the fact the treatment could be performed outside the major exhaust stream so not affecting the engine back pressure, it will affect the economy of the control system. This treatment period must be minimised for commercial viability; this could be achieved by optimisation of the treatment conditions as well as variation of the catalyst composition.

We wish to thank the University, AECl and FRD for financial support and Dr R. Copperthwhite (AECl) for encouragement and discussions during the course of the work.

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Received, 10th June 1996; Com. 6/04043H