An investigation of catalysts for the on board synthesis of NH_3. A possible route to low temperature NO_x reduction for lean-burn engines

J.P. Breen [a], R. Burch [a,]*, and N. Lingaiah [b]

[a] School of Chemistry, Queen's University Belfast, David Keir Building, Stranmillis Road, Belfast BT9 5AG, N. Ireland
[b] Catalysis Laboratory, Indian Institute of Chemical Technology, Hyderabad, 500 070, India

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Platinum group metal catalysts have been investigated for the formation of NH_3 from $NO + H_2$ at low temperatures in the absence and presence of CO. Although CO inhibits the formation of NH_3, substantial amounts are still observed with a Pt catalyst. By combining Pt with a support (ceria–zirconia) that has low temperature NO_x storage characteristics it has been shown in transient experiments that NH_3 can be formed and stored *in situ* under rich conditions, and may then be used to reduce NO_x under lean burn conditions.

KEY WORDS: platinum metal catalysts; NO_x reduction; lean-burn; ammonia storage.

1. Introduction

The development of fuel efficient lean-burn gasoline engines has resulted in major new challenges for emission control systems that are now required to satisfy the current environmental legislation. The release of nitrogen oxides ($NO + NO_2$, commonly referred to as "NO_x") is a particular problem because the excess oxygen in the exhaust of a lean-burn engine precludes the use of conventional three-way catalyst technology. Direct NO_x reduction under lean-burn conditions was first attempted by using the residual hydrocarbons (mainly propene) in the exhaust. Many hundreds of catalyst formulations were screened but none were acceptable. When this use of residual hydrocarbons proved unsuccessful, the direct addition of a hydrocarbon reductant (such as the gasoline itself) into the exhaust in front of the catalyst was tried. Although this provided substantially greater levels of NO_x reduction in laboratory experiments the general consensus is that this is still not a technically viable approach. Consequently, for gasoline engines the so-called "Toyota concept" in which NO_x is stored in the catalyst under lean conditions and the NO_x trap is regenerated by a short period under rich conditions, has found favour [1]. In Europe, however, there is still an issue with NO_x traps because they are poisoned by sulphur oxides [1–5], and European gasoline still contains too high a level of sulphur to allow these NO_x traps to be used for long periods of time.

In the case of diesel engines the NO_x removal problem is further constrained because the sulphur level, even in "low sulphur diesel", is still much higher than in gasoline. Moreover, the temperature of the diesel exhaust is significantly lower than in the case of a gasoline engine. Consequently, the kinetics of NO_x trapping, which requires oxidation of NO to NO_2 as a first step [6,7], and regeneration, which requires decomposition of barium nitrate species, are barely adequate. Indeed, in the case of small diesel engines fitted with turbochargers, the temperature of the exhaust under urban driving conditions can be well below 200 °C, which may be contrasted with the >500 °C typically found with gasoline engines.

For heavy duty diesel engines, there is a growing interest in using NH_3 to reduce NO_x, with the NH_3 being produced on board a vehicle by the hydrolysis of a urea solution [8]. This approach derives from well-established technology for stationary applications (*e.g.* large power stations) where it is known that by judicious choice of catalyst it is possible to get an acceptable rate of reduction of NO_x at low temperatures [9]. Furthermore, as compared with the NO/hydrocarbon reaction, there is much less tendency to produce nitrous oxide (N_2O), itself a hazardous greenhouse gas, as a by-product of the NH_3/NO_x reaction. In the NO/hydrocarbon case, at temperatures below about 250 °C, N_2O is the major product [10].

Richter *et al.* [11] have proposed using a zeolite to trap ammonia gas that can then be used for NO_x reduction at low temperatures. However, using NH_3 storage for mobile applications is not ideal because this still requires regular replenishment of the reservoir. Consequently, the possibility of generating NH_3 *in situ* from the NO_x in the exhaust has been advocated [12]. In this paper we present some preliminary results on the formation of NH_3 on Platinum Group Metal catalysts at low temperatures, and the subsequent attempt to use this NH_3 to reduce NO_x.

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* To whom correspondence should be addressed.

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2. Experimental

Catalysts, nominal composition 1% by weight, were prepared by incipient wetness impregnation of the oxide support (SiO_2 or CeO_2-ZrO_2) using aqueous solutions of Pt(II) DNDA, palladium nitrate, or rhodium nitrate). The prepared catalysts were dried at 120 °C overnight and then calcined at 500 °C for 2 h.

The activity of the various catalysts for the reaction between NO and H_2, in the absence or presence of CO, were investigated using a flow microreactor with on-line analysis by mass spectrometry. 100 mg catalyst was prereduced in 3%H_2/He at 400 °C for 2 h and then exposed to a reaction mixture of 1000 ppm NO, 1000 ppm H_2 in a He flow of 200 $cm^3\,min^{-1}$, giving a gas hourly space velocity of 120 000 h^{-1}. Results were obtained by analysis of reactants and products as the temperature of the catalyst bed was raised from ambient to 450 °C at a ramp rate of 5 °C min^{-1}. The effect of CO on the formation of NH_3 was investigated by adding CO at the levels of 200 or 1000 ppm.

To investigate the feasibility of producing NH_3, which could then be captured by the catalyst for subsequent reduction of NO_x, pulse experiments were conducted in which NO (500 ppm) and O_2 (5000 ppm) were passed over the 1%Pt/CeO_2-ZrO_2 catalyst at 200 °C. The flow of O_2 was cut off temporarily every 5 min and replaced by H_2 (2000 ppm) for 30 s.

3. Results and discussion

Figures 1–3 show the results of the NO/H_2 reaction with the silica-supported catalysts. With Pt/SiO_2, NH_3 is first observed at relatively low temperatures (<100 °C). NH_3 is the major nitrogen-containing product from 120 to *ca.* 350 °C, and the concentration increases up to a maximum at around 200 °C. In the case of Pd/SiO_2, NH_3 is only observed above 150 °C and reaches a plateau at *ca.* 320 °C where it remains the major nitrogen-containing product at all temperatures. The Rh/SiO_2 catalyst produces the smallest amount of NH_3 with formation first being observed at around 150 °C, followed by a flat maximum at *ca.* 270 °C before the concentration declines again.

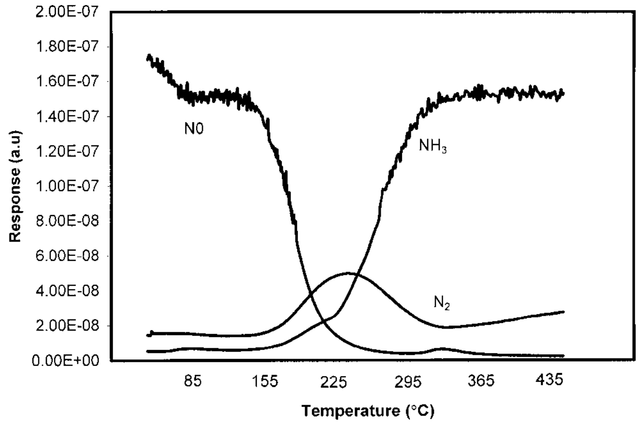

Figure 2. NO + H_2 reaction over 1%Pd/SiO_2. (Reaction conditions: total gas flow: 200 ml/min; catalyst weight: 0.100 g; NO: 1000 ppm; H_2: 2000 ppm; He: balance).

Since the Pt/SiO_2 catalyst gives the highest concentration of NH_3 at the lowest temperature, the effect of CO was investigated. Figure 4 (compare also figure 1) shows that addition of CO has a significant effect on reducing the ability of the Pt to produce NH_3. Thus, adding only 200 ppm CO raises the temperature at which NH_3 is detected from *ca.* 50 °C to about 125 °C, and adding 1000 ppm CO raises this temperature further to *ca.* 170 °C. However, even in the presence of CO, the formation of NH_3 is substantial.

To investigate whether any NH_3 formed through the NO/H_2 reaction could be trapped and used for subsequent reduction of NO_x, we selected a 1%Pt/CeO_2-ZrO_2 catalyst that in other work had been found to capture NO_x at low temperatures. Figure 5 shows that this material also produces substantial amounts of NH_3 in the NO/H_2 reaction at temperatures from

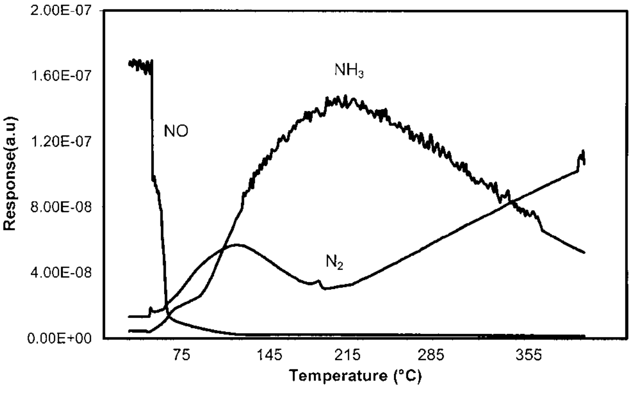

Figure 1. NO + H_2 reaction over 1%Pt/SiO_2. (Reaction conditions: total gas flow: 200 ml/min; catalyst weight: 0.100 g; NO: 1000 ppm; H_2: 2000 ppm; He: balance).

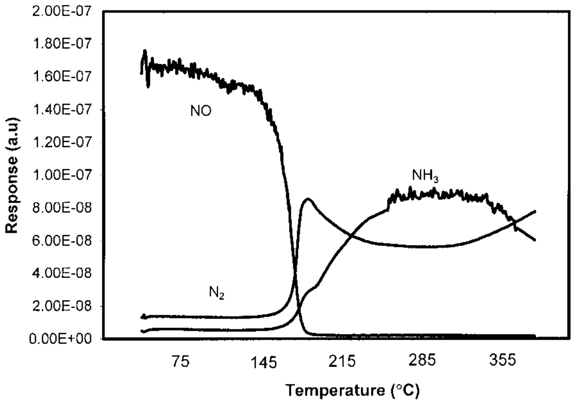

Figure 3. NO + H_2 reaction over 1%Rh/SiO_2. (Reaction conditions: total gas flow: 200 ml/min; catalyst weight: 0.100 g; NO: 1000 ppm; H_2: 2000 ppm; He: balance).

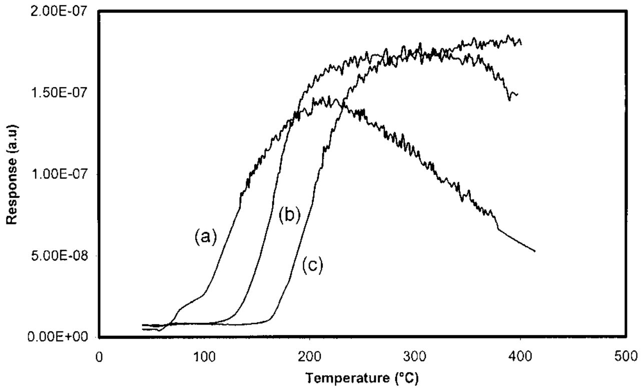

Figure 4. $NO + H_2 + CO$ reaction over 1%Pt/SiO_2: effect of CO concentration. (Reaction conditions: total gas flow: 200 ml/min; catalyst weight: 0.100 g; NO: 1000 ppm; H_2: 2000 ppm; CO: 200–1000 ppm; He: balance). (a) no CO; (b) CO: 200 ppm; (b) CO: 1000 ppm.

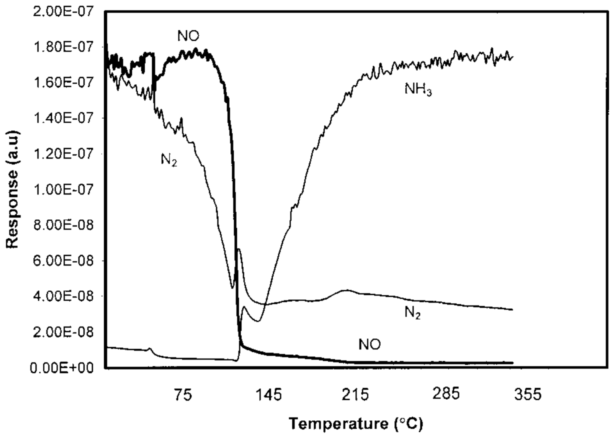

Figure 6. $NO + H_2 + CO$ reaction over 1%$Pt/CeO_2/ZrO_2$ catalyst. (Reaction conditions: total gas flow: 200 ml/min; catalyst weight: 0.100 g; NO: 1000 ppm; H_2: 2000 ppm; CO: 500 ppm; He: balance).

100 °C upwards with a broad peak at around 200 °C. Moreover, when CO (500 ppm) was added, figure 6 shows that although there is a drop in the production of NH_3 at lower temperatures, the formation at 200 °C is still substantial.

This 1%Pt/CeO_2-ZrO_2 catalyst was selected, therefore, to test the concept that NH_3 could be formed under rich conditions from NO and H_2 and that this NH_3 could be used to react with NO_x under lean conditions. Figure 7 shows the results of these pulse experiments. During the period when the O_2 is flowing, the NO concentration gradually increases but as soon as the O_2 is replaced by H_2 the NO concentration first increases, presumably due to desorption of NO_x stored under lean conditions, and then decreases before slowly rising again during the lean period.

The most significant result, however, is the observation that the formation of N_2 is observed for about 70 s even though the H_2 is only present for 30 s. Thus, when the lean conditions are re-established, N_2 is produced for about 40 s after the reductant is flushed from the system. Figure 7 shows that during this period the NO level decreases while NH_3 is simultaneously observed. Since there is no way in which NH_3 could be produced from NO in the *absence* of H_2 we conclude that the NH_3 peak must arise from the formation of NH_3 while H_2 is present. Furthermore, the observation of an NH_3 desorption peak *after* removal of the H_2 suggests that the NH_3 has indeed been stored on the catalyst. Thus, it seems clear from these transient experiments that NH_3 can be formed *in situ*, trapped, and used to reduce NO_x.

In summary, the formation of NH_3 from NO and H_2 at moderate temperatures has been demonstrated on Pt, Pd and Rh catalysts. In pulse experiments, it has been further shown that the outlet concentration of NO is

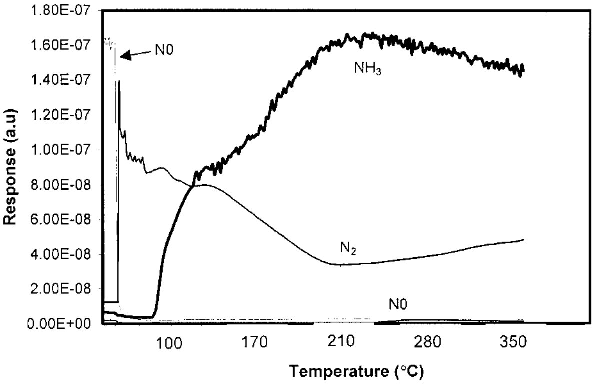

Figure 5. $NO + H_2$ reaction over 1%$Pt/CeO_2/ZrO_2$ catalyst. (Reaction conditions: total gas flow: 200 ml/min; catalyst weight: 0.100 g; NO: 1000 ppm; H_2: 2000 ppm; He: balance).

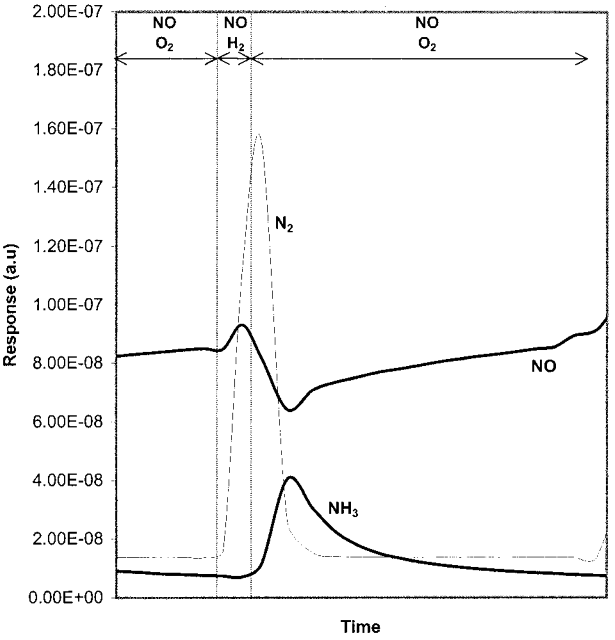

Figure 7. $NO + O_2$ reaction with H_2 pulse over 1%$Pt/CeO_2/ZrO_2$ catalyst. (Reaction conditions: total gas flow: 200 ml/min; catalyst weight: 0.100 g; NO: 500 ppm; O_2: 0.5%; H_2: 2000 ppm; He: balance; reaction temperature: 300 °C).

lowered in transient experiments in which NH_3 is observed. It is concluded that it would be possible, in principle, to use these catalysts to form NH_3 *in situ* and then to use this NH_3 to reduce NO_x at low temperatures under lean conditions.

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