

# The Platinum Catalysed Reduction of Nitric Oxide by Ammonia

## A SOLID ELECTROLYTE POTENTIOMETRY AIDED STUDY

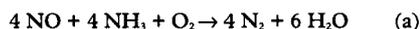
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*The reduction of nitric oxide by ammonia on platinum catalysts has been investigated in the temperature range 300 to 400°C at reactant partial pressures between 0.05 and 5 mbar. During a combined potentiometric and kinetic study, a discontinuous change in both the reaction rates and the surface state has been observed at a partial pressure ratio for nitric oxide:ammonia of 1.5. If ammonia is in excess in the gas phase then nitric oxide is directly reduced to nitrogen. However, an excess of nitric oxide leads to a strong formation of nitrous oxide, and the nitrogen formation thus proceeds via nitrous oxide.*

Selective catalytic reduction by ammonia is commonly used to decrease the nitrogen oxides emissions which are discharged as stack gases from power station and industrial boilers. In large scale commercial applications, in Japan and Germany, catalysts based on vanadium oxide and titanium oxide are generally used (1, 2). Nevertheless, the use of platinum catalysts has also been proposed (3); indeed, the very first observation that ammonia can be used as a selective reducing agent for nitric oxide in the presence of oxygen reported the use of platinum (4). However, there are only a few studies of the reaction kinetics, and in particular kinetic measurements made on polycrystalline platinum at ambient pressure are rather scarce.

In the presence of oxygen the stoichiometry of the main reaction may be written as follows:



Side reactions to be avoided are the formation of nitrous oxide and the oxidation of ammonia by oxygen. As the oxygen is involved in the reduction of nitric oxide (a), the oxygen activity in the catalyst on stream is an essential parameter of the system. This activity can be measured by a potentiometric method based on the application of solid ion conductors (5).

Therefore, we have carried out a combined

potentiometric and kinetic investigation of the reduction of nitric oxide by ammonia on polycrystalline platinum, starting with measurements made in the absence of oxygen. In this case the following reactions have to be considered, first the reduction of nitric oxide to nitrogen or nitrous oxide:



and then, potentially, the further reduction of nitrous oxide:

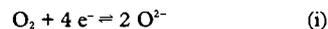


## Experimental Work

During the combined potentiometric and kinetic measurements the catalytically active surface also acts as one electrode of the galvanic cell:

reactants/electrode//solid electrolyte//electrode/air  
(measuring side) (reference side)

the potential determining reaction:



takes place at the boundary of the three phases, namely gas-electrode-electrolyte. Therefore, a highly porous electrode is required. This was

prepared from a platinum paste consisting of a fine metallic powder (Pt No. 00863, Johnson Matthey Alfa Products) suspended in a viscous organic matrix of polyvinyl acetate and ethylacetoacetate. During a suitable heat treatment the organic matrix is burned off in air, leaving the metallic sponge.

The set-up used for making the potentiometric measurements is depicted in Figure 1. The open circuit potential,  $\Delta E$ , was determined and the oxygen activity at the catalyst,  $a_{O_2}$ , was evaluated via the Nernst equation:

$$\Delta E = \frac{R \cdot T}{4 \cdot F} \ln \frac{a_{O_2}}{P_{O_2}^R} \quad (\text{ii})$$

where  $P_{O_2}^R$  denotes the oxygen partial pressure on the reference side of the cell. The basic assumptions of the method have been discussed in detail elsewhere (5, 6).

The reaction cell is part of a recirculation loop which includes a membrane pump, as shown schematically in Figure 2. The system is open to the atmosphere, its recirculation volume being 78.5 cm<sup>3</sup>. The recirculation ratio  $\frac{V}{V_0}$  has a value between 15 and 25, and is held constant throughout one series of measurements. The dotted lines show the boundaries of the control volume. The reaction rate,  $r'_i$ , is obtained via the mass balance of the open system in a stationary state. It is related to the catalyst surface:

$$r'_i = \frac{1}{F} \cdot \frac{d\xi_r}{dt} \quad (\text{iii})$$

where the subscript r represents the specific rates of Reactions (b) to (d), and  $\xi$  is the corresponding extent of the reaction. The concentrations of nitric oxide, nitrous oxide and ammonia are determined by non-dispersive infrared spectrometry; the oxygen content may be measured by means of a magnetic device. The controlled total volume flow is obtained by use of a soap bubble flow meter. The combined kinetic and electrochemical measurements can be summarised as follows:

**Control variables:** reactant concentration  $c_i$ , temperature T

**Measured quantities:** potential difference  $\Delta E$ , reaction rates  $r'_i(c_i, T)$  as a function of the con-

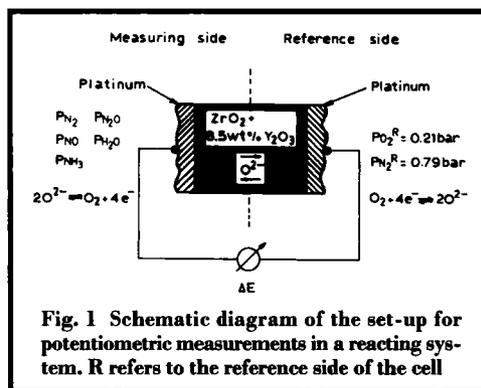


Fig. 1 Schematic diagram of the set-up for potentiometric measurements in a reacting system. R refers to the reference side of the cell

centration of species  $i$ , and temperature T  
**Derived quantity:** oxygen activity,  $a_{O_2}$  at the catalyst surface.

## Results

The reaction has been investigated in the temperature range 300 to 400°C. Measurements were made at a constant temperature, and with one reactant at a constant partial pressure of 0.5 mbar, while the partial pressure of the second reactant was increased sequentially from 0.05 to 5 mbar. All results were obtained under stationary conditions. The stationary state was attained, by definition, when the variation in the gas phase concentrations was less than 1 per cent and the variation in the potential difference was less than 5 mV over a 30 minute period.

Typical results obtained during the nitric oxide reduction are shown in Figures 3 and 4. In the Figures the rates of nitrogen,  $r'_b$ , and nitrous oxide,  $r'_c$ , formation, and the oxygen activity at the catalyst surface,  $a_{O_2}$ , are plotted against the nitric oxide partial pressure in Figure 3, and against

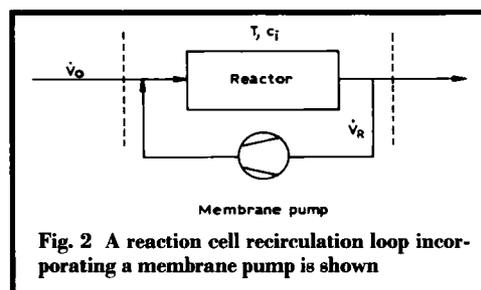


Fig. 2 A reaction cell recirculation loop incorporating a membrane pump is shown

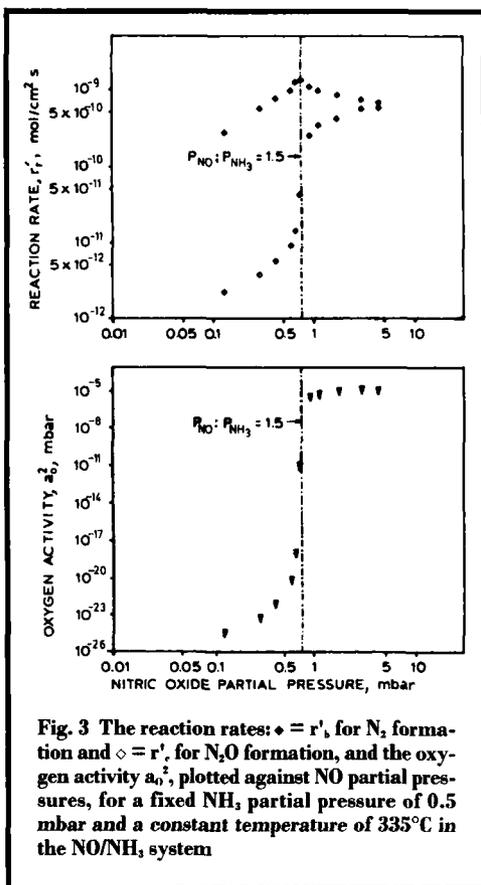


Fig. 3 The reaction rates:  $\blacklozenge = r'_1$  for  $N_2$  formation and  $\circ = r'_1$  for  $N_2O$  formation, and the oxygen activity  $a_{O_2}$ , plotted against NO partial pressures, for a fixed  $NH_3$  partial pressure of 0.5 mbar and a constant temperature of 335°C in the NO/ $NH_3$  system

the ammonia partial pressure in Figure 4. The discontinuity of the reaction order in both the nitrogen and nitrous oxide formation rates has been confirmed by all results. It occurs at the same ratio of the nitric oxide to ammonia partial pressures, that is 1.5, and is independent of the fact that the measurements are made by varying either the nitric oxide or the ammonia partial pressures. It can be seen from Figure 4 that the rates are only slightly affected by temperature in the domain examined; nitrous oxide formation is increased somewhat at lower temperatures.

Following the partial pressure dependence of the oxygen activity,  $a_{O_2}$ , a sharp discontinuity is again observed when the ratio of the partial pressures is 1.5. Furthermore, it is shown that at low values of oxygen activity the nitrous oxide formation rate is about two orders of magnitude lower than the nitrogen formation rate, whereas

both rates are of the same magnitude in the region of high oxygen activity.

Therefore it was also interesting to investigate the reduction of nitrous oxide by ammonia. The experiments were carried out in the same way as described above, keeping the partial pressure of one reactant constant. The results are depicted Figure 5, showing the reduction rate,  $r'_d$ , and the oxygen activity as a function of the ammonia partial pressure. The results are quite similar to those obtained in the nitric oxide reduction study. The reaction rate shows the same transition from positive to zeroth order, as shown in Figure 4, accompanied by the sharp discontinuity in the oxygen activity at the surface. The high values of the nitrous oxide reduction rate in the

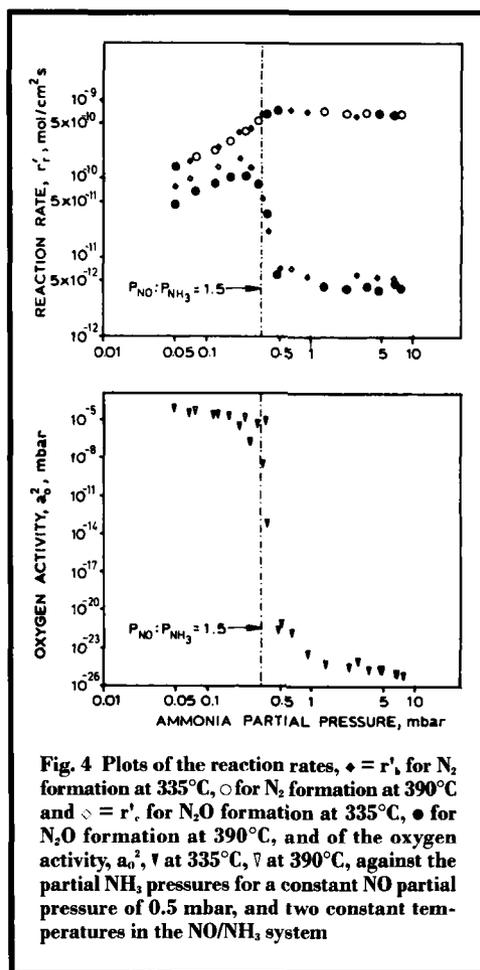


Fig. 4 Plots of the reaction rates,  $\blacklozenge = r'_1$  for  $N_2$  formation at 335°C,  $\circ$  for  $N_2$  formation at 390°C and  $\bullet = r'_1$  for  $N_2O$  formation at 335°C,  $\bullet$  for  $N_2O$  formation at 390°C, and of the oxygen activity,  $a_{O_2}$ ,  $\blacktriangledown$  at 335°C,  $\triangledown$  at 390°C, against the partial  $NH_3$  pressures for a constant NO partial pressure of 0.5 mbar, and two constant temperatures in the NO/ $NH_3$  system

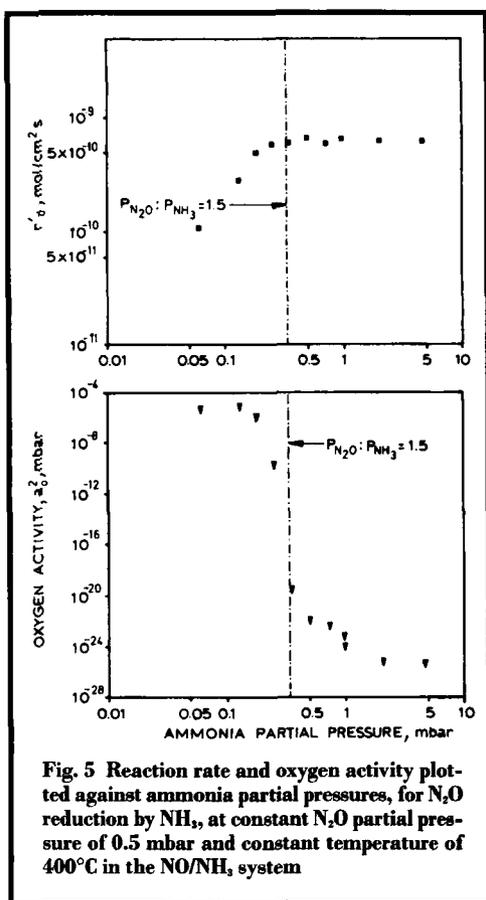


Fig. 5 Reaction rate and oxygen activity plotted against ammonia partial pressures, for N<sub>2</sub>O reduction by NH<sub>3</sub>, at constant N<sub>2</sub>O partial pressure of 0.5 mbar and constant temperature of 400°C in the NO/NH<sub>3</sub> system

reducing atmosphere ( $P_{N_2O}:P_{NH_3} < 1.5$ ), seen in Figure 5, are thus correlated to low values of the nitrous oxide formation rate, seen in Figure 4.

## Discussion

We have verified that the measured reaction rates are not influenced by outer or inner mass transfer effects. The results are consistent, the same values being obtained when the partial pressures of nitric oxide and ammonia are each 0.5 mbar, independent of the experimental procedure, that is increasing the partial pressure of ammonia or of nitric oxide. The measurements are reproducible within the limits of experimental precision.

A comparison of the results with data from the literature is limited because no measurements have been made under really comparable con-

ditions; either the pressure range or the form of the catalyst, and always the experimental procedure, are different. We can only compare the turnover frequencies reported, even if that mode of quantification is somewhat ambiguous, since it conceals the different pressure ranges used. In the low temperature range studied in the present work, the reported turnover frequency data attain values up to 100 (7), lie between 0.1 and 10 (8) or only between 0.03 and 0.5 (9). However, the influence of structure sensitivity cannot be ruled out, as Takoudis and Schmidt have used polycrystalline platinum wires (7), Somorjai and co-workers have used polycrystalline platinum foils (8), and Katzer and co-workers have used 1 weight per cent platinum on alumina (9). Our values do not exceed 1, and therefore compare favourably with the data obtained on dispersed supported platinum. Thus at least our results do not contradict the literature reported so far.

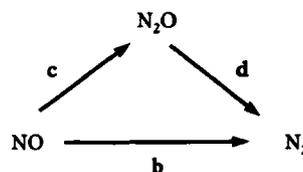
If we return to the results obtained in the nitric oxide/ammonia system, it is interesting to look at the observed selectivities,  $S$ , calculated using Equations (iv) and (v):

$$S_N = \frac{\xi_b}{\xi_b + \xi_c} \quad (iv)$$

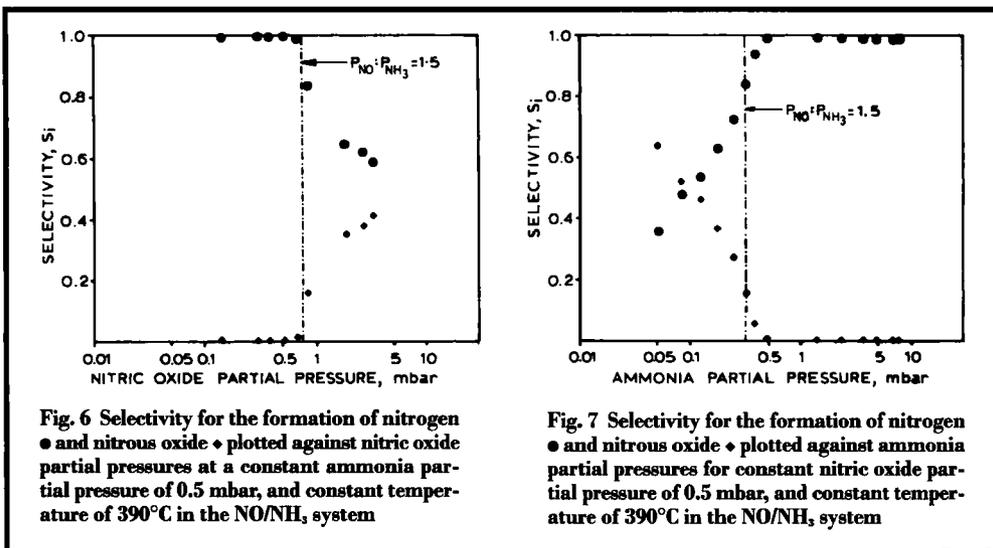
$$S_{N_2O} = \frac{\xi_b}{\xi_b + \xi_c} \quad (v)$$

Typical values are plotted in Figures 6 and 7. It is clearly seen that in a reducing atmosphere, where  $P_{NO} < 1.5P_{NH_3}$ , the selectivity of nitrogen formation practically equals 1, and that the nitrous oxide formation remains negligible. In an oxidising atmosphere, however, the selectivity of nitrous oxide formation may exceed 0.5.

As nitrous oxide may in turn be reduced by ammonia we can represent the reacting system by a triangular scheme:



Thus the question arises whether the high selectivity of nitrogen formation, observed under



conditions of excess ammonia, is due to the fact that the nitrous oxide formation rate is low, or that the nitrous oxide reduction rate is very high? At the moment we cannot answer this question quantitatively, but we can get an indication by using the results obtained in the separate measurements of the nitrous oxide reduction. Let us assume, as a rough approximation, that the reduction of nitrous oxide is not influenced by the presence of nitric oxide, that is, the reaction of the two nitrogen oxides can be superposed. Then we can calculate, at least at a constant ammonia partial pressure of 0.5 mbar, the rate of the nitrous oxide reduction (Reaction d) in the nitric oxide/ammonia system, and thus obtain the amount of nitrogen formed in step d,  $\dot{n}'_{N_2,d}$ . In Figure 8 the ratio of  $\dot{n}'_{N_2,d}$  and the total amount of nitrogen formed in the nitric oxide/ammonia system,  $\dot{n}'_{N_2,total}$ , is plotted as a function of the partial pressure of nitric oxide. It is clearly shown that under reducing conditions the nitrogen formation proceeds exclusively through the direct reduction of nitric oxide (path b in the Scheme), since  $\dot{n}'_{N_2,d}/\dot{n}'_{N_2,total}$  is less than 0.1, whereas under oxidising conditions the nitrogen formation is merely due to paths b and d.

It is interesting to correlate the observed behaviour with the oxygen activity at the catalyst surface. At very low values of  $a_{O_2}$  we find a high

selectivity to nitrogen, while at higher values vigorous nitrous oxide formation occurs, and between the two domains a discontinuous variation of reaction order, selectivity and oxygen activity is observed. This may be explained by the postulation of two different states of the surface: if  $P_{NO} > 1.5 P_{NH_3}$  the surface is covered by oxygen or an oxygen containing species, whereas it is in a reduced state if the reducing compound is predominant in the gas phase.

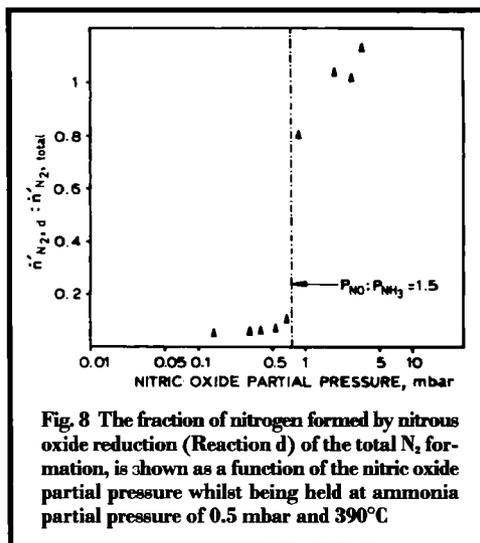


Fig. 8 The fraction of nitrogen formed by nitrous oxide reduction (Reaction d) of the total  $N_2$  formation, is shown as a function of the nitric oxide partial pressure whilst being held at ammonia partial pressure of 0.5 mbar and 390°C

Using this interpretation we can foresee the effect of the presence of oxygen in the gas phase. In the case of noble metal catalysts, gas phase oxygen cannot but increase the oxygen activity at the surface. This had already been shown in the oxygen/nitric oxide/carbon monoxide system (6). We therefore expect that the presence of oxygen will mainly increase the rate of nitrous oxide formation and suppress its further reduction to nitrogen. In that case the observed acceleration in the nitric oxide conversion rate by oxygen, reported in several studies (4, 9–12), would merely be due to an increased nitrous oxide formation, which has already been observed (9, 11). This point of view is further supported by the fact that under

high vacuum conditions the addition of oxygen does not accelerate the nitric oxide conversion (13), since under these conditions the domain of high oxygen activity at the surface cannot be attained.

Preliminary results obtained in the three reactant system ammonia/nitric oxide/oxygen have already confirmed the estimated influence of gas phase oxygen.

#### Acknowledgements

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## Cobalt-Platinum Alloys as Recording Media

The magneto-optical properties of both cobalt/platinum multilayer and alloy thin films have been widely discussed in the literature, and abstracts of such reports have appeared here on numerous occasions. At infrared wavelengths cobalt/platinum multilayers exhibit a similar signal level to that of TbFeCo, the material currently used in magneto-optic recording products, and recently it has been demonstrated that at wavelengths close to 450 nm cobalt/platinum displays a clear advantage. Despite the potential importance of these materials, little work on this alloy system has been reported. Now, however, a communication from the IBM Research Division, Almaden Research Center, San Jose, California, considers in detail the dependence of the perpendicular magnetic anisotropy in cobalt-platinum alloy films on their composition (D. Weller, H. Brändle, G. Gorman, C.-J. Lin and H. Notarys, *Appl. Phys. Lett.*, 1992, 61, (22), 2726–2728).

By means of electron beam evaporation in an

ultra-high vacuum system, alloy films were prepared on fused silica and silicon substrates, at temperatures between 150 and 350°C. Both co-evaporation and subatomic layering of 0.1 nm layers were employed, the latter technique enabled the film compositions to be reproduced conveniently. Binary cobalt-platinum alloy films consisting of about 20 to 40 atomic per cent cobalt were found to have large perpendicular magnetic isotropy, appropriate Curie temperatures, 100 per cent perpendicular remanence and coercivities of the order of 200 kA/m. Also the static magneto-optical signal given by reflectivity, Kerr rotation and Kerr ellipticity was found to be enhanced compared to those of cobalt-platinum multilayers or of TbFeCo.

The combination of magnetic and magneto-optical properties, the potentially high chemical stability and the ease of manufacture make 25 nm cobalt-platinum alloy films (45 to 90 per cent platinum) highly attractive for short wavelength magneto-optic storage.