

Low-temperature catalytic decomposition of N₂O on platinum and bismuth-modified platinum: identification of active sites

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Classification of the active surface sites of platinum catalysts responsible for low temperature N₂O decomposition, in terms of steps, kinks and terraces, has been achieved by controlled addition of bismuth to as-received platinum/graphite catalysts.

The concept of active centers was introduced by Taylor many years ago¹ and even at that early stage it was recognized that the site requirements for a catalysed reaction could be quite specific. Atoms at corners, edges or in close-packed planes could be expected to have different activities. However, since it is difficult to isolate the different types of atoms in small metal particles, for many reactions it has proved difficult to identify the active site requirements on real catalysts. In principle, if specific sites on a metal particle can be blocked then it should be possible to determine whether these sites had different activities and, if so, whether they were catalytically important. Bismuth-modified Pt catalysts offer just such an opportunity.

Nitrous oxide (N₂O), which is a serious environmental hazard,^{2–4} is formed when the emissions from diesel or petrol engines are passed through catalytic converters at low temperatures. With Pt-based catalysts, there has been debate^{5–9} as to whether this N₂O is an intermediate in the reduction of NO to N₂ which, if correct, would require that N₂O decomposition was a relatively facile reaction on Pt even though Pt catalysts are less active than Rh for N₂O decomposition.^{8,10–12} In the case of NO decomposition on Pt there is conflict within the literature as to whether flat surfaces¹³ or stepped surfaces¹⁴ are more active. Clearly, it would be useful to know for N₂O decomposition on Pt whether the preferred active site was also a close-packed surface since this would influence the design of new catalysts.

The base catalyst used in this study was 5% Pt/C (Johnson-Matthey; metal dispersion 15.2% (H₂ chemisorption), pre-reaction metal surface area 1.88 m² g⁻¹, Pt particle diameter 7.43 nm). Surface modification using bismuth is by irreversible adsorption of aqueous bismuth ions¹⁵ from a 7.2 × 10⁻⁴ M solution of bismuth nitrate. 1 g of catalyst was stirred with 7, 15 or 22.5 cm³ of the bismuth solution for several hours followed by rinsing with pure water and drying at 353 K for 12 h. 100 mg samples were placed in a Pyrex tube and held in place between two quartz wool plugs. A thermocouple was positioned in the catalyst bed to monitor temperature and the reactor furnace was controlled using a Eurotherm 818 controller. The reactant gases, He (100%, BOC Gases), N₂O (0.2% in He, BOC Gases), H₂ (3% in He, BOC Gases) were introduced using Aera mass flow controllers. Reaction products were monitored using a computer interfaced Fisons Gaslab 300 Mass Spectrometer, operated using the corresponding Thermosoft software. Prior to N₂O pulsing, the catalyst was reduced in 10000 ppm H₂/He for 30 min, and then flushed in He prior to cooling to room temperature. Since Bi will thermally desorb from the platinum over the temperature range 400–1000 °C,¹⁶ it was necessary to perform this reduction at 300 °C. Characterisation of the catalysts was achieved using H₂ and CO chemisorption (Micromeritics Autochem 2910) and cyclic voltammetry. The electrochemical cell and procedure used for collecting cyclic voltammetry data has been described previously.^{15,17} All

potentials are quoted relative to a saturated palladium–hydrogen electrode in contact with the 0.5 M sulfuric acid electrolyte. All bismuth surface coverages are quoted in terms of the fraction of Pt sites blocked as measured by the ratio of electroadsorption peak intensity of bismuth modified surface to that of the clean surface (one monolayer of bismuth corresponds to all hydrogen adsorption sites blocked).

Fig. 1 shows cyclic voltammetry data for the unmodified and bismuth surface modified catalysts. The increase in bismuth loading is signified by a gradual loss in intensity of all peaks in the potential range 0–0.6 V. A similar approach of controlled dosing of adatoms on to the surface of a platinum catalyst using cyclic voltammetry to monitor surface coverage has been reported in the extensive review article by Lamy-Pitara and Barbier.¹⁸ Our approach differs from theirs only in that spontaneous deposition rather than underpotential deposition of the bismuth adatom was employed. The cyclic voltammetry, by comparison with results from single crystal samples, shows for the fresh Pt catalyst a predominantly stepped surface ({110}-peak at 0.05 V > {100}-peak at 0.2 V). Although there is some terracing ({100}-broad feature between 0.25 and 0.35 V and {111}-broad peak centred at 0.47 V) this appears to have relatively short-range order.¹⁹ This catalyst also exhibits a fairly high number of defect sites (kinks) as signified by the broadness of the defect peaks relative to the much sharper peaks observed for single crystals containing linear steps.²⁰ The Bi 0.4 /Pt catalyst, in accordance with the known adsorption behaviour of Bi on Pt (*i.e.* kinks blocked before steps²¹), shows a partial blockage of the {100} and {110} defect sites. {100} terraces are also slightly affected but {111} terrace density remains virtually unchanged. The Bi 0.6/Pt catalyst shows continued adsorption of Bi at both step sites (all defect peak intensity has been lost) whilst coverage at terrace sites remains virtually unchanged from the previous sample. The onset of bismuth adsorption on (111) terraces is signified by the appearance of a characteristic surface redox peak at 0.55 V.¹⁵ The chemisorption data (Table

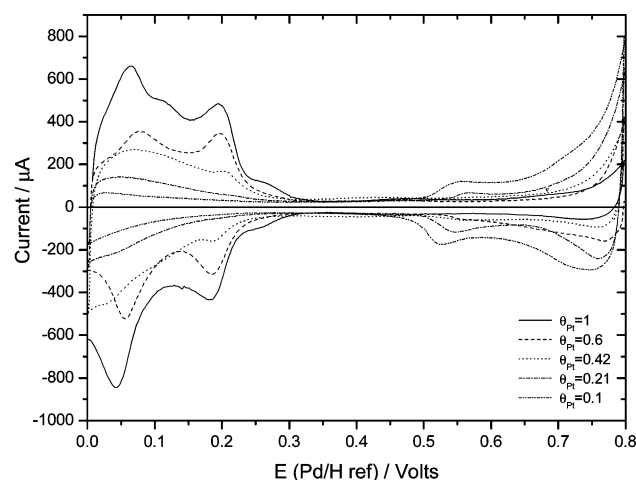


Fig. 1 Cyclic voltammograms for Bi modified and unmodified catalysts.

Table 1 Characterisation details for the catalysts. Bismuth monolayer coverage was determined by cyclic voltammetry. Metal dispersion and the corresponding coverages were determined by H₂ (a) and CO (b) chemisorption

Catalyst	Bi coverage (from c.v.)/ML	Pt dispersion (%)	Calculated Bi coverage/ML
5% Pt/C	0	15.24 (a) 14.72 (b)	0
Bi/5% Pt/C	0.4	9.29 (a) 10.09 (b)	0.39 (a) 0.31 (b)
Bi/5% Pt/C	0.6	9.03 (a) 7.68 (b)	0.41 (a) 0.48 (b)

1) show in both cases that around 40% of the Pt is covered by Bi.

The catalytic results show a startling effect of this partial coverage of Pt by Bi. Fig. 2 shows that N₂O conversion at 25 °C occurs with slowly decreasing effectiveness on a pure Pt catalyst. The decline in conversion is due to self-poisoning by O_(ads) under these experimental conditions. However, both Bi-modified catalysts show a dramatic loss of activity and zero conversion of N₂O is observed after very few pulses. It is emphasised that the loss of N₂O decomposition activity coincides precisely with the blocking of all defect sites.

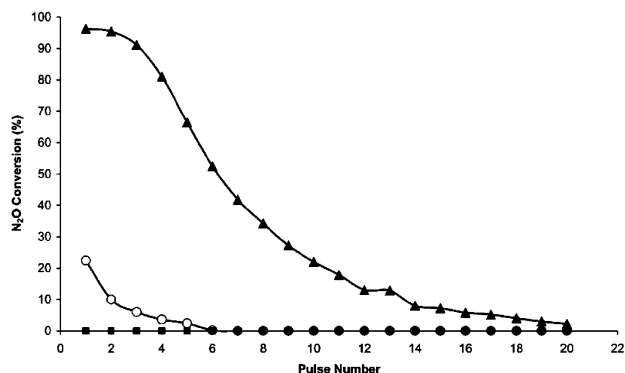


Fig. 2 N₂O decomposition over 5% Pt/C, with and without bismuth coverage. (▲) 5% Pt/C, (○) 0.4 ML Bi/5% Pt/C, (■) 0.6 ML Bi/5% Pt/C, under standard reaction conditions (100 mg catalyst, 2000 ppm N₂O pulses in He, total flow 50 cm³ min⁻¹).

In conclusion, Pt catalysts modified in a controlled way with Bi have been used to identify the active centers on Pt for N₂O decomposition. It seems clear that terrace sites are not active for this reaction. In contrast, edge or defect sites appear to be the active sites so that, in contrast to NO dissociation on Rh, where large metal particles are favoured, we conclude that the highest activity for N₂O dissociation on Pt will occur on very small metal particles.

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