

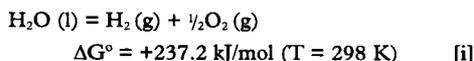
An Interfacial Mediator Interpretation of Noble Metal Electrocatalysis

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Electrocatalysis is of considerable interest in many areas, such as in energy conversion and storage, electroanalysis, water purification and electroless metal deposition, and some of the most active materials in this area are the noble metals and their oxides, for example platinum and ruthenium dioxide. It is widely accepted that (even in heterogeneous catalysis in general) there is a wide gap between theory and practice: most industrial catalysts are developed by repetitive testing techniques. It has been proposed by the author that the fundamental problem in this area is the fact that the active interfacial mediators in electrocatalysis, which are the adatoms and incipient hydrous oxide species, reside virtually outside the solid lattice and exhibit chemical – and especially redox – behaviour very different to that of well embedded surface species. There is an urgent need to develop and apply highly sensitive techniques to investigate the behaviour of such quite low coverage reactive surface/interfacial species.

Electrocatalysis is concerned largely with methods – usually based on the choice and state of the electrode material – for increasing the rate of a desired electrode reaction at a specific potential or, alternatively, lowering the overpotential (and hence the energy requirement) for a given rate of reaction (1–3). As in all forms of catalysis, the operation of an electrocatalyst is based on the provision of an alternative route for reaction, one that has a lower energy of activation than that of the same process in the absence of the electrocatalyst. Electrocatalysis may be viewed as a subsection of heterogeneous catalysis which currently has far more widespread applications and has been more extensively investigated. However, there are important differences (1), one of which is the fact that cell processes (electrode reactions always occur in pairs – oxidation at the anode and reduction at the cathode) are frequently “uphill” from a thermodynamic viewpoint, for example:

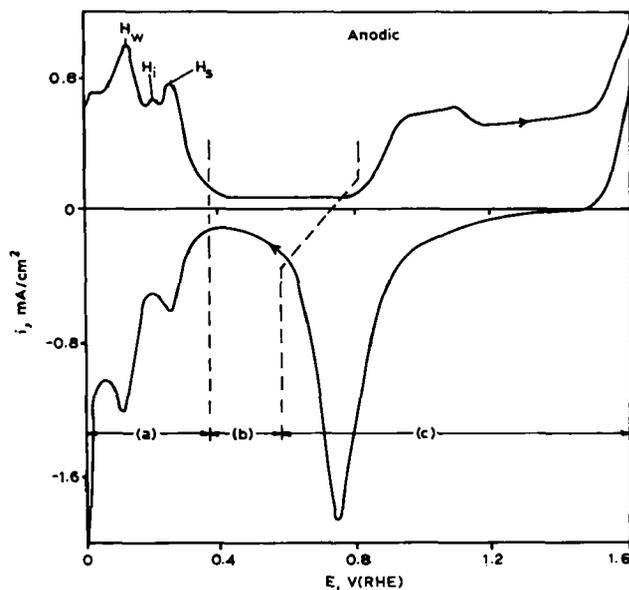


The water electrolysis cell used to carry out such a reaction may be regarded simply as a con-

venient device for adding the extra energy (in electrical form) needed to convert the reactants to the higher energy products. Such a system based on the reaction shown in Equation [i] forms the basis of a very interesting future energy strategy. Solar energy may be converted (in photocells) to electrical energy and then (in electrolysis cells) to chemical (that is, hydrogen) energy. The hydrogen may be piped elsewhere, stored, and then used on demand, with oxygen from the air, to produce electricity in a quite efficient manner in a hydrogen/oxygen fuel cell whose operation is based on the reverse of the reaction shown in Equation [i]. This intermediate production of hydrogen (or perhaps a metallic hydride) is the basis of a remarkably clean, carbon dioxide-free approach to future energy demand that is worthy of greater attention: a 350 kW energy conversion and storage system, based on this approach, is currently in operation in Saudi Arabia (4).

The role of electrocatalysts in such energy conversions systems is a crucial one as the processes involved in both the electrolyser and fuel cell must occur both rapidly (thus reducing plant size and capital cost) and efficiently – with minimum

Fig. 1 Typical cyclic voltammogram (0 – 1.60 V, 50 mV/s) for a bright polycrystalline platinum electrode in 1.0 mol/dm³ H₂SO₄ at 25°C. Such a response is usually subdivided into 3 regions (5): (a) formation/reduction of adsorbed hydrogen, (b) double layer charging/discharging, and (c) formation/removal of surface oxide (or OH_{ads} and O_{ads} species) – the latter process exhibits hysteresis. Peaks H_w and H_s (positive sweep) are attributed to the oxidative removal of weakly bound and strongly bound hydrogen, respectively. The explanation of the intermediate (H_i) peak is a matter of some controversy (14)



energy loss. The demands on the electrocatalysts, in terms of activity, long term stability and cost, are quite severe and platinum metals play a vital role in several of the processes involved.

In-situ Changes in Surface Activity

An important factor with regard to the operation of an electrocatalyst is that these materials usually operate in contact with an electrolyte. A solvent such as water is not inert, it frequently interacts not only with the other reactants or intermediates at the interface but also with the electrode (or the electrocatalyst) itself. It is well established for instance that with platinum (an efficient electrocatalyst for many reactions) in aqueous media (5) hydride (or H_{ads}) or oxide (OH_{ads} and O_{ads}) films are formed on the metal surface over certain ranges of potential, see Figure 1. It is generally accepted that, as is clear from Figure 1, oxygen gas evolution at a platinum anode surface (which usually occurs well above the reversible potential for this reaction, 1.229 V(RHE) at T = 298 K) occurs not at the metal but at the oxide-coated metal surface (1). The solvent is not the only species that can react with, and modify the reactivity of, the sur-

face of the electrocatalyst – so also can electrolyte anions such as Cl⁻, SO₄²⁻ or HSO₄⁻, adventitious impurities and organic reactants. For example in the oxidation of methanol, at the anode of a direct methanol/air fuel cell, at low pH the process of interest is complete conversion according to the following reaction:



However, this process tends to be severely inhibited due to the accumulation of a CO_{ads} poisoning species produced at the interface via the following type of side reaction (6):



Other alterations in the electrocatalyst that may occur in practice include dissolution – resulting (with multicomponent systems) in surface enrichment phenomena – and sintering (which results in loss of true surface area and surface density of active sites).

The Gap between Theory and Practice

A rather disconcerting feature in the area of heterogeneous catalysis in general is the presence of a wide gap between theory and practice.

Thus, Bond has pointed out recently that "Reflections on the research carried out in the field of heterogeneous catalysis over the last four decades will show not so much a catalogue of problems solved as of problems shelved" (7). At approximately the same time Schlögl claimed that "All the catalytic processes vital to industry were developed by purely empirical methods and countless screening experiments" and "Our understanding of the relationship between structure and reactivity is inadequate" (8). The situation with regard to electrocatalysis is not different; the empirical nature of this area was pointed out earlier by Pletcher who also stated that "there remains a gulf between those who developed electrode materials and those who seek to understand the physical chemistry of electrocatalysis" (9).

A major factor contributing to the lack of understanding may well be insufficient attention devoted to defect centres or active sites at solid surfaces. A typical bulk metal such as platinum or gold has a well characterised 3-dimensional lattice structure – and the surface is frequently envisaged as a planar termination of such a lattice. Such a surface is easier to comprehend and model (as compared with its defect counterpart) and considerable attention has been devoted in recent years to producing, and investigating the activity of such single crystal plane electrode surfaces (10). They are obviously excellent substrates for investigation by newly developed high resolution microscopy (for example scanning tunnelling and atomic force (11)) techniques. The problem is the major gap (discussed by Schlögl (8)) between single crystal plane surfaces and those used in practice, for example platinum dispersed at quite low coverage, as an electrocatalyst, on carbon at the cathode of a fuel cell. The ill-defined surface of the metal in such a state is not easily modelled and as is clear, for instance from a recent conference proceedings on electrode/electrolyte interfaces, the role of defects, at a fundamental level, is widely ignored at present (12). This is quite surprising as the "active site" concept, originally proposed by Taylor, has been well established in the empirical interpretation of heterogeneous catalysis for many years (13).

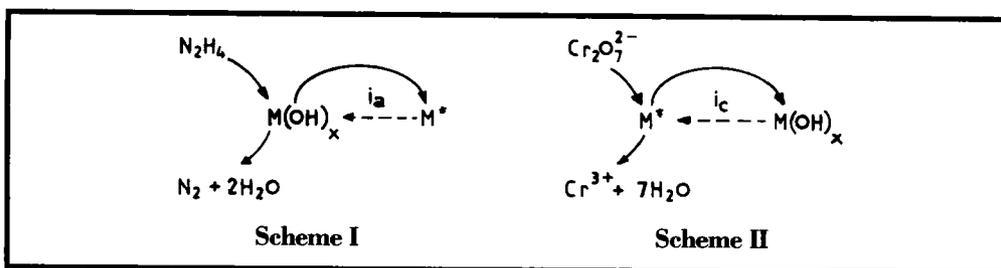
A further complication in electrocatalysis is the possibility that low co-ordination surface metal atoms exhibit significantly different redox behaviour as compared with their high co-ordination equivalents at the same surface. The basis of this approach, which was discussed in some detail in a recent controversial paper from this laboratory (14), is supported by the following statement by Adamson (15):

"Not all atoms on the surface [of a solid] are equivalent in nature; those present at ragged asperities are more energy-rich than those with a normal number of nearest neighbours and possess a higher than average surface energy and surface mobility".

Low co-ordination, energy-rich, surface metal atoms are unusual in several respects. Firstly, because of the lack of crowding at the surface, these atoms react with solvent molecules (or other species) in an unusually rapid manner. Secondly, these less crowded atoms, on oxidation, can co-ordinate more oxygen or hydroxide species and hence may form hydrous, rather than anhydrous, oxides. Finally, because the reactive metal atoms (the reduced form of the couple) are energy (or activity)-rich, they generally oxidise at a lower potential than high co-ordination surface metal atoms in a process known as premonolayer oxidation. As already discussed earlier (14) anomalous oxidation is an independently established feature of the reaction of supported platinum clusters with gaseous oxygen (16). The formation of low coverage hydroxy species on gold in base at premonolayer potentials has already been established using Surface Enhanced Raman Spectroscopy (SERS) (17). Unfortunately, SERS does not yield precise information as to the identity of the product and the technique is applicable, to a large extent, only to the Group I(b) metals (gold, silver and copper).

A Revised View of Noble Metal Electrochemistry

As pointed out in an earlier review, hydrous oxides are now known and have been investigated for most of the noble, and several non-noble, metals (18). They are best regarded as



a distinct series of compounds (14) that differ from their regular, anhydrous, oxide or hydroxide equivalents in that they frequently exhibit poor structural regularity combined with high redox activity; the latter is particularly evident in systems such as iridium, rhodium, iron and nickel hydrous oxides (18) where intermediate redox transitions, for example those between the II/III or III/IV oxidation states (of the same cation), are involved.

It is assumed that all real metal surfaces contain poorly stabilised, high energy, atoms; these may be concentrated at unusual sites, such as tips of asperities, or occur in a random manner (due to thermal vibrations) on the surface. Normally the coverage of such species is quite low and both the electrochemical and spectroscopic responses due to their oxidation is usually quite weak. As mentioned here earlier there is spectroscopic (SERS) evidence for the formation of hydroxy species on gold in base at low potentials. All noble metals are assumed to exhibit such premonolayer oxidation behaviour and – although the evidence is not yet conclusive – the correlation (as discussed here below) between hydrous oxide electrochemistry and the electrocatalytic behaviour of the noble metals, both with regard to oxidation and reduction processes, is impressive.

From an historical viewpoint the conventional view of noble metal surface electrochemistry – hydrogen, double layer and oxide region in the case of platinum or double layer and oxide region in the case of gold – received early acceptance. However, while such an interpretation is evidently valid for the relatively well stabilised surface metal atoms (the vast majority of such atoms at the interface), it does not take into account

the redox behaviour of the very minor coverage of energy-rich, poorly lattice stabilised, surface metal atoms. The low responses for the latter (as they undergo anomalous oxidation – at potentials well below that for the onset of regular monolayer formation) is evident in certain instances, for example silver (19) and gold (20); the premonolayer response for the latter is sometimes attributed (21) – incorrectly in the view of the author (and especially in view of the SERS data) – to the oxidation of impurities.

The recent claim (14) that premonolayer oxidation of platinum occurs within the hydrogen adsorption region may be controversial, but the observation of enhanced premonolayer oxidation of both platinum (22) and gold (23), plus charge displacement (24) from the hydrogen adsorption to the double layer region of platinum in acid (following prolonged polarisation at low potentials), clearly shows that the basic electrochemistry of the noble metals is more complex than is generally assumed.

The Incipient Hydrous Oxide/Adatom Mediator Model of Electrocatalysis

The Incipient Hydrous Oxide/Adatom Mediator (IHOAM) model of electrocatalysis (14) is based on the assumption that the low coverage (or incipient) hydrous oxide, $M(OH)_x$, formed in the premonolayer oxidation process, is the effective oxidant (or mediator) in electrocatalytic oxidation processes, see Scheme I, whereas the low co-ordination surface metal atom, M^* , is the effective reductant (or mediator) in electrocatalytic reduction processes, see Scheme II.

According to these schemes the mediator is restored to its initial state by externally supplied

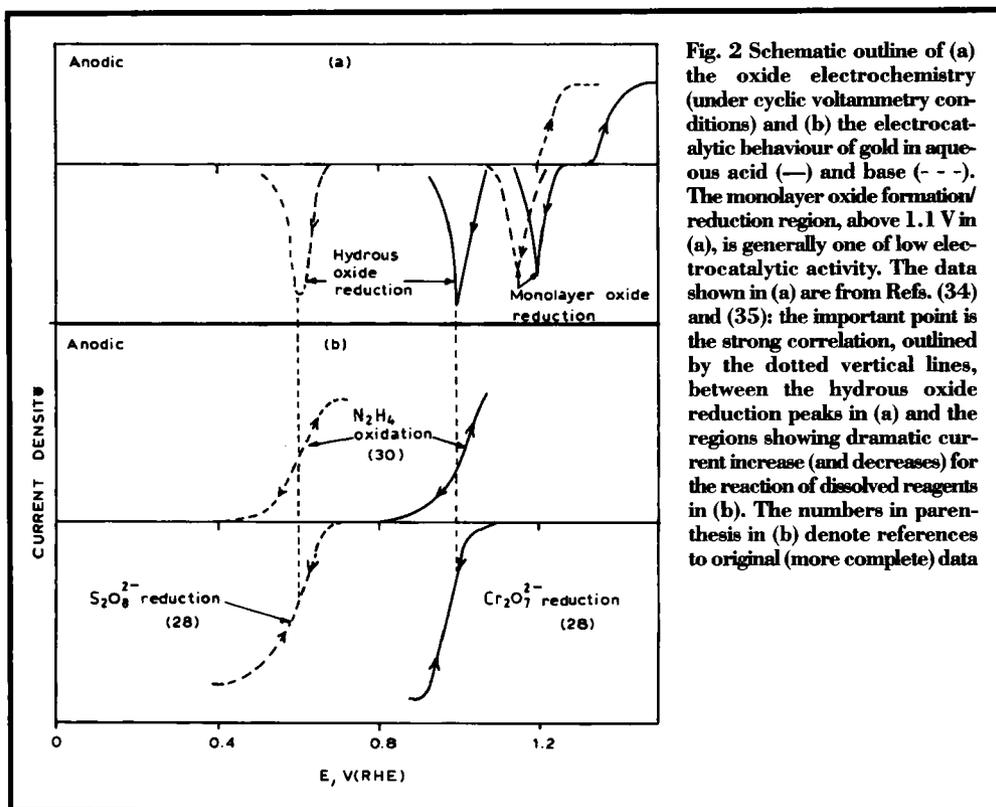


Fig. 2 Schematic outline of (a) the oxide electrochemistry (under cyclic voltammetry conditions) and (b) the electrocatalytic behaviour of gold in aqueous acid (—) and base (- - -). The monolayer oxide formation/reduction region, above 1.1 V in (a), is generally one of low electrocatalytic activity. The data shown in (a) are from Refs. (34) and (35); the important point is the strong correlation, outlined by the dotted vertical lines, between the hydrous oxide reduction peaks in (a) and the regions showing dramatic current increase (and decreases) for the reaction of dissolved reagents in (b). The numbers in parenthesis in (b) denote references to original (more complete) data

anodic (i_a) or cathodic (i_c) current, that is electrocatalysis involves an interfacial cyclic redox transition between two unusual states – the low co-ordination surface metal atom and the incipient hydrous oxide.

The above approach (which is controversial) has been outlined in considerable detail recently for both gold (25) and platinum (14). Significant support is provided by the data summarised in Figures 2 and 3. A schematic outline of the oxide (including the hydrous oxide) electrochemistry of gold in aqueous media is given in Figure 2(a): a more detailed account (including an explanation of the shift in the hydrous oxide/metal transition to a lower potential on increasing the solution pH) of the behaviour of this system has been published (14, 25). It is clear from Figure 2(b) that numerous electrocatalytic oxidation and reduction processes commence and terminate in the region of the active metal/hydrous oxide transition. Similar data is

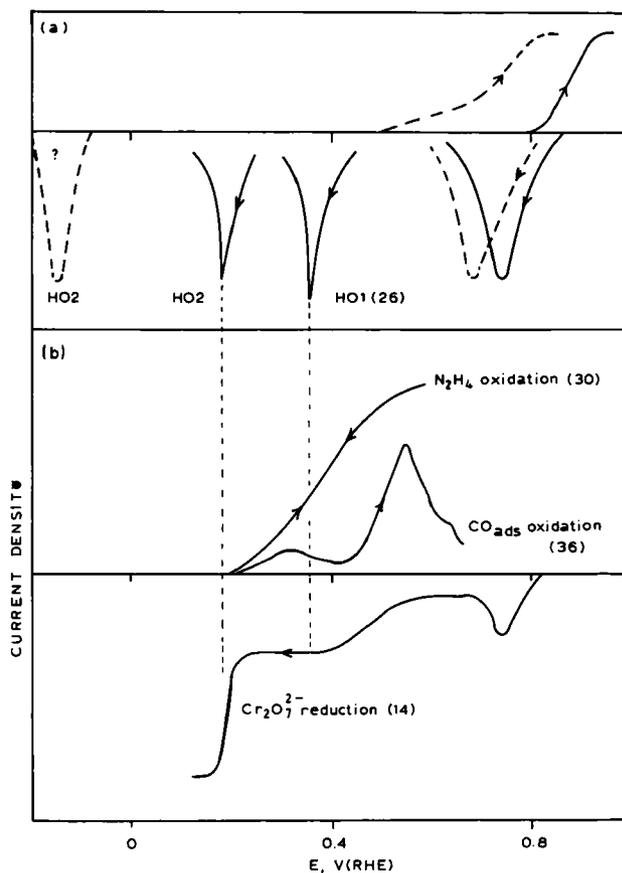
shown in Figure 3 for platinum – an account of novel aspects of the oxide electrochemistry of this metal has been published (26, 27).

Some general points concerning the data in Figures 2 and 3 are noteworthy:

- [1] For many electrocatalytic oxidation processes the formation of the regular monolayer oxide deposit leads to inhibition of the reaction.
- [2] In a given system, for instance gold in acid, there is a switch in the process being catalysed, for example from dichromate reduction at low potentials to hydrazine or oxalic acid oxidation at high potentials on sweeping through the active metal/incipient hydrous oxide transition region (28).

This is quite understandable in terms of a change in oxidation state of the interfacial mediator with potential: such results highlight the fact that the cessation of reaction of a bulk solution species, for example dichromate reduction on the positive sweep, is not due to surface

Fig. 3 This is the equivalent diagram (to Figure 2) for platinum in aqueous acid (—) and base (---). Reduction of the hydrous (HO2) oxide in base is surprisingly difficult at room temperature (27) – this (plus the monolayer region above 0.6 V) is largely ignored here. Again, as with gold, the increases in current for the oxidation or reduction of solution species occur in the regions close to the hydrous oxide, HO1 and HO2 (26), peaks. Such behaviour is masked or complicated by surface deactivation in the case of organic oxidations, that is the latter processes rarely occur on clean platinum surfaces



deactivation – and only the IHOAM approach rationalises the changeover potential value and the variation of the latter with solution pH. Kinetic theories based on this approach have been developed for both metals (14, 19) and oxides (29).

[3] The region of onset of high electrocatalytic activity in the case of platinum (and gold) is far removed from that of monolayer oxide (or OH_{ads} and O_{ads}) formation. In two of the cases shown here for platinum in acid, CO_{ads} oxidation and $\text{Cr}_2\text{O}_7^{2-}$ reduction, there are two regions of significant current increase – coinciding approximately with the potentials for the two platinum hydrous oxide (HO2 and HO1 (26)) reduction processes, that is two distinct mediators (or inhibiting species) appear to be involved – again

such a result is explicable only in terms of the IHOAM approach. The highly anomalous behaviour of the HO2 oxide of platinum in base was discussed at length in a recent publication (27). It is worth noting that the oxidation of a wide range of reactive organics also commences at around 0.2 V(RHE) on platinum in acid providing that steps are taken (for example use of a pulsing technique) to minimise the effect of deactivating CO_{ads} species (30).

Conclusions

The major role of active sites or surface irregularities in determining both the catalytic and electrocatalytic activity of surfaces is widely accepted (31, 32). Such sites are frequently regarded in terms of co-ordinatively unsaturated

surface atoms (or groups (33)) but precise details with regard to structure and electronic properties of such species are generally not available (32). The novelty of the present approach is that it assumes (largely on the basis of the considerable knowledge now available on noble metal hydrous oxide behaviour, correlations between this and electrocatalysis – see Figures 2 and 3, and SERS data for gold (17)) that low co-ordination surface metals or groups exhibit a significantly different type of redox behaviour as compared with that of similar but high co-ordination number surface species.

A major practical problem in this area is the difficulty in detecting, and investigating the properties of, the quite low coverage, relatively labile, species involved. In addition, there is a range of practical considerations, for example it would obviously be useful to investigate methods for the

optimisation of the activity, effective coverage (which is not necessarily the maximum coverage) and long term stability of a particular mediator.

Finally, the concept of activated chemisorption should not be discarded. In some instances, such as hydrogen gas evolution on platinum, this may well be the sole mechanism of reaction. In other cases, such as methanol oxidation at a platinum/ruthenium-activated anode (3), the electrocatalyst may operate in a bifunctional manner – the alcohol may be activated by chemisorption on platinum sites while the ruthenium functions as the oxygen transfer agent (to produce carbon dioxide). The active platinum atom may still undergo an intermediate redox transition in the course of the latter reaction, that is there may be an intermediate transfer of an oxygen species (derived from water) from a ruthenium to a platinum centre.

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Control of Emissions of Nitrogen Oxides

Environmental Catalysis: ACS Symposium Series 552

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This volume contains papers given at a symposium sponsored by the Catalysis and Surface Science Secretariat at the 205th National Meeting of the American Chemical Society, held in Denver, Colorado, from 28th March to 2nd April 1993. Although the symposium covered a number of aspects of environmental gaseous pollution from mobile and stationary sources, the principal emphasis was on control of nitrogen oxide (NO_x) emissions, and work was reported on platinum group metal based catalysts, notably containing platinum, palladium and rhodium.

Approximate molecular orbital computations of adhesion and nitric oxide (NO) reduction for rhodium, palladium and platinum monolayers on the (0001) faces of oxygen and aluminium of α -alumina, were reported by T. R. Ward, P. Alemany and R. Hoffmann (Cornell University) who concluded that the support significantly affects the Fermi levels of the composite system, which in turn affects the NO adsorption mode. They suggest that the platinum-oxygen interface is particularly suited for both dissociative adsorption and coupling of two adsorbed nitrosyls, yielding a reduced form of N₂O₂.

The state of platinum-rhodium catalysts during three-way catalysis continues to be important. B. E. Nieuwenhuys and J. Siera (Leiden University) and K.-I. Tanaka and H. Hirano (University of Tokyo) presented a joint paper on differences in behaviour of platinum, rhodium and platinum-rhodium surfaces towards NO reduction. Silica was chosen to minimise support effects; experiments were performed with synthetic gas mixtures. They concluded that the catalytic properties depend strongly on the gas phase composition and temperature, and on the composition of the platinum/rhodium particles. Under oxidising conditions and at temperatures above 600 K, rhodium segregates to the surface; but under reducing conditions, platinum-rhodium alloy particles are reformed. This significantly influences the reactions of NO with both carbon monoxide (CO) and hydrogen, since rhodium is generally a better catalyst than plat-

inum for the CO/NO reaction, while platinum is better for the hydrogen/NO reaction. Thus the predominant mechanism for NO removal depends on catalyst surface composition.

Infrared studies performed by G. Srinivas, S. S. C. Chuang and S. Debnath (University of Akron) on the interaction of NO and CO on rhodium/silica and cerium-rhodium/silica clearly show the formation of rhodium-NCO and silicon-NCO as the predominant species during the CO/NO reaction at 723 K. However, isotopic studies under steady state conditions indicate that these species are "spectator" species rather than the principal reaction intermediates.

Palladium-only catalysts were compared with platinum, rhodium and platinum/rhodium systems for three-way control in closed loop controlled motor vehicles, by J. C. Summers and W. B. Williamson (Allied Signal). While palladium has significantly better hydrocarbon control, its NO_x performance, especially under rich operating conditions, tends to be adversely affected by lead and sulphur. This can be overcome by developing palladium catalysts less sensitive to these poisons, or by combining separate palladium only and platinum/rhodium catalysts in multibrick systems, leading to converters containing varying amounts of all three metals, depending on car calibration and fuel quality.

While most papers discussed NO reduction, the effects of sulphated platinum/zirconia catalysts in NO and sulphur dioxide (SO₂) oxidations were reported by J. R. H. Ross and co-workers, (University of Twente). The sulphated catalyst had higher activity in both reactions, but increased selectivity for NO. A similar increase in NO selectivity occurred after ageing platinum/zirconia in a NO/SO₂/oxygen gas mixture, and sulphate could be detected on the aged catalyst. These effects are ascribed to changed surface acidity modifying adsorption strength.

Despite the papers being at least 18 months old, they are still a valuable addition for the design of catalytic systems to meet the emission limits set for the next decade. D.E.W.