

The Origins of Nobility

THE SPECIAL CHARACTERISTICS OF THE PLATINUM METALS

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Last October the 11th Swedish Symposium on Catalysis was held at Lund University on the theme of "Precious Metals as Catalysts, and Possible Alternatives". In an invited lecture the author explored the origins of the catalytic activity of the platinum group metals and, although dismissing the possibility of complete imitation, speculated on ways in which their electron densities might be slightly but advantageously modified. The following article is a summary of his lecture.

The incorruptibility of gold has fascinated mankind down the centuries, and is responsible for its widespread use for coinage, jewellery and objets d'art which have on occasion survived prolonged periods in inhospitable environments. The quality of gold was of course well known to the ancients. The recognition that there exist other metals of similar nobility and even greater usefulness is more recent; these are of course the platinum group metals. Their widespread applicability has prompted many to ask whether their good properties can be imitated. In this short review we consider the chemical and physical basis of nobility and of catalytic activity, and what the prospects are for their more economic use or for improvement to their properties.

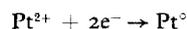
The Physicochemical Basis of Nobility

Nobility is epitomised by resistance to oxidation and corrosion. Electropositive metals such as sodium readily lose their

valency electrons to become cations having a closed outer electron shell. Thus sodium reacts vigorously with water:



The ease with which the valence electron is lost is reflected by the large negative value of the standard reduction potential and by the low value of the first ionisation potential of the gaseous atom. Values of these and other physical constants referred to in this section are to be found in the Table. The conversion of the metal to its oxide is dangerously exothermic because of the great stabilisation resulting from the transfer of electrons from metal to oxygen. At the other extreme platinum, which has a large **positive** standard reduction potential for the process



is quite unreactive towards water under ambient conditions, and has a large first ionisation potential. The properties of gold are similar. Concerning the oxides, platinumous oxide (PtO) has a small negative heat of formation, while auric oxide (Au_2O_3) is thermodynamically unstable.

The great differences between sodium and platinum are qualitatively accounted for by the different ways in which their outermost electrons are employed in bonding in the metallic state. The one valence electron of sodium is shared between eight nearest neighbours, so sodium is soft and plastic, and has a low latent heat of sublimation. Electrons in orbitals of lower energy are inviolate and do not participate in bonding. In the case of platinum however all the *d*-electrons are involved in cohesive bonding, in a manner which defies simple description. For this reason its



Fig. 1 Because of its great resistance to oxidation at high temperatures, in addition to its high catalytic activity, platinum—in the form of rhodium-platinum gauze here seen being woven—is employed in the production of nitric acid by the oxidation of ammonia, a process operating at around 850°C

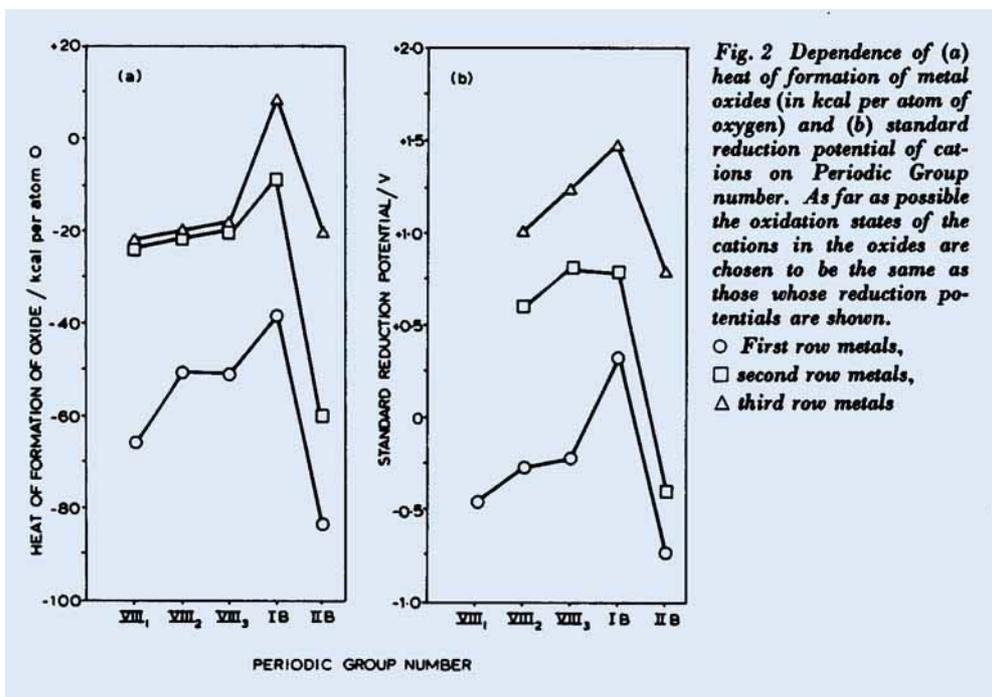
oxidation to the platinumous state is difficult, the metal is hard, and the latent heat of sublimation is higher. Analogous statements may also be made in the case of gold.

So far we have only considered the extremes of nobility and baseness. As in society there are degrees in both. Figure 2 shows the values of the standard heats of formation of the oxides of the metals in Groups VIII, IB and IIB, and the standard reduction potentials of their positive ions, plotted against Periodic Group number. There is the expected close parallelism between the two quantities. In each transition series “nobility” increases to a maximum in Group IB, and also increases on moving down each group. There is no clear demarcation between noble and base metals; one useful criterion is however that only those metals showing a standard reduction potential of less than -0.4 V will

react with water at pH 7 and 25°C. Of the metals shown in this Figure, only iron, cadmium and zinc fall in this category. Cobalt and nickel, which are usually labelled base metals, are “nobler” than iron, which explains their useful addition to iron to produce corrosion-resistant alloys.

The Usefulness of Nobility

The noble metals win pride of place in the hierarchy of metals because of the wide range of applications which their properties allow them to have. Space does not permit an extensive recapitulation of these, which have in any event frequently been described in this journal. Instead we focus attention on their catalytic behaviour. The outstanding catalytic properties of metals manifest themselves in two distinctly different sets of conditions. First, at temperatures at or not very much



greater than room temperature, they may be used in a liquid medium: here activity and selectivity are of prime importance. Second, they may be used in gaseous reactions at temperatures much above ambient (500 to 900°C): here if the atmosphere is an oxidising one the resistance of the metal to oxidation is of over-riding importance. In both sets of conditions the platinum group metals are

widely but not exclusively employed. The reason for their choice under high temperature oxidising conditions such as ammonia oxidation (Figure 1 shows the manufacture of gauzes for this application), odour abatement and vehicle exhaust treatment in preference to other base metals should be evident from what has gone before. Under reducing conditions their inability to form bulk carbides

Comparison of Some of the Properties of Sodium, Gold and Platinum			
	Sodium	Gold	Platinum
Standard reduction potential/V	-2.71 (Na ⁺ → Na ⁰)	+1.42 (Au ³⁺ → Au ⁰)	+1.20 (Pt ²⁺ → Pt ⁰)
First ionisation potential of gaseous atom/eV	5.14	9.22	8.97
Standard heat of formation of oxide/kcal per atom of oxygen	-120.6 (Na ₂ O)	+6.4 (Au ₂ O ₃)	-17 (PtO)
Latent heat of sublimation/kcal mol ⁻¹	25.8	84.9	135
Young's modulus/kg mm ⁻²	0.03	0.88	1.70
Vickers Hardness	0.1	20	40

Fig. 3 At lower temperatures, between 250 and 450°C, platinum-containing catalysts are widely used in petroleum reforming. Modern developments in the use of promoters have increased the stability and extended the life of such catalysts



in the presence of hydrocarbons permits their use for a range of conversions which are central to petroleum reforming (Figure 3).

The Source of the Catalytic Activity of the Platinum Group Metals

We must now examine the reason for their high activity in the low temperature region. It has long been appreciated that, for a catalytic reaction to occur between two reactants, at least one must be chemisorbed by the catalyst surface, and in most cases both must be chemisorbed simultaneously. The only important molecule not chemisorbed by all the platinum metals is nitrogen; only ruthenium and osmium so act. This means that only they are capable of catalysing ammonia synthesis. They are probably more active than iron, although no precise measurements are available to validate this statement: the use of promoted iron is probably preferred for economic and historic reasons. All the platinum metals readily chemisorb all other reactants of common interest. But so do the

“base” metals: why then do the platinum metals show greater catalytic activity?

The answer to this question becomes clear when we appreciate that in any reaction system there is an optimum **strength of adsorption** for the reactants. If the chemisorbed molecules are bound too strongly to the surface, they will be unreactive towards each other, and in the extreme limit the reaction will be self-poisoned. On the other hand if they are not adsorbed strongly enough, they will be unable to cover sufficient of the surface and the reaction rate will be low for this reason. Thus if the rate were to be plotted against some parameter measuring the strength of adsorption, we should expect it first to rise and then after passing through a maximum to fall again. For a system comprising two reactants the ideal catalyst is one for which the two reactants are about equally strongly adsorbed, and with a strength just sufficient to achieve full surface coverage at the reaction temperature.

We now have to examine the factors which

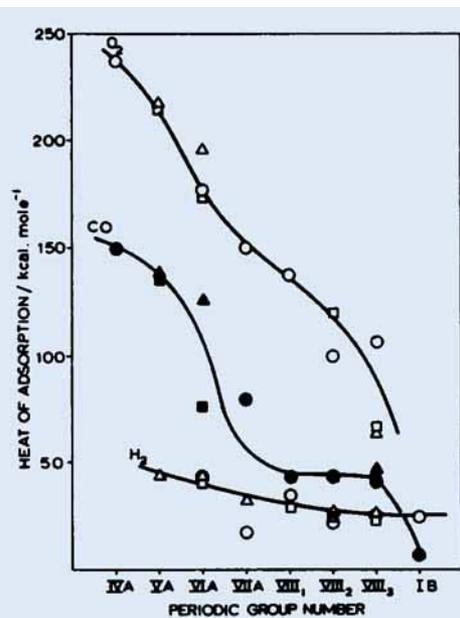


Fig. 4 Initial heats of adsorption of oxygen, carbon monoxide and hydrogen as a function of Periodic Group number.

- First row metals,
- second row metals,
- △ third row metals

affect the strengths of adsorption of typical reactants on metal surfaces. The strength can be quantitatively measured by the heat released when chemisorption occurs, namely by the heat of adsorption. Extensive information is available on the heats of adsorption of oxygen, carbon monoxide and hydrogen especially on evaporated films of metals, and these are plotted as a function of Periodic Group number in Figure 4. In each case there is a significant decrease on moving from left to right, and in Group VIII the values shown by the platinum group metals tend to be lower than those for the corresponding base metals. The distinction is particularly clear in the case of oxygen on nickel, palladium and platinum. It has to be remembered that the bond strength will affect the activation energy of a reaction and will thus appear in an exponential term, so that a difference of only a very few kilocalories in heat of adsorption can lead to a

significant difference in rate. We have thus come close to the heart of the problem: the platinum group metals evidently owe their high catalytic activity to the lower strengths with which molecules are chemisorbed on their surfaces. We must now ask whether this analysis can be taken further.

It was noticed some time ago that there is a reasonable correspondence between the heats of adsorption of oxygen and the heats of formation of the most stable oxides (1). This suggests that the chemisorbed oxygen layer closely resembles a two-dimensional oxide phase, and that similar factors determine the stabilities of both. This analogy cannot however be taken further, since not all the metals of interest form bulk hydrides with whose stability the heat of adsorption of hydrogen might be compared, and only few of these metals form simple carbonyls, so that a comprehensive comparison with the heats of adsorption of carbon monoxide cannot be drawn. It is noteworthy that the base Group VIII metals form simple carbonyls ($\text{Fe}(\text{CO})_5$, $\text{Co}_2(\text{CO})_8$ and $\text{Ni}(\text{CO})_4$), whereas the platinum metals form only carbonyl halides or polymeric cluster carbonyls, but highly unstable simple carbonyls of some of the platinum metals have recently been characterised at very low temperatures (2). It has however been noted (3) that the heats of adsorption of all three gases are linearly related to the heats of formation of the bulk oxides, a generalisation sometimes referred to as the Tanaka-Tamaru Rule. Since these heats of adsorption also decrease monotonically with increasing Periodic Group number, at least up to Group IB, this may conveniently be used as the parameter reflecting strength of adsorption.

These concepts can now be tested against the published measurements for the activities of a number of silica-supported metals for the hydrogenation of ethylene (4). In Figure 5 the rates are plotted on a logarithmic scale versus Periodic Group number. Two important conclusions can be drawn from this figure. (i) Rates for the second and third

transition series are similar, but greater than those for the corresponding base metals, and (ii) in each group the rate is greatest in the region where the heat of adsorption of hydrogen is a minimum (see Figure 4). The activities of silver and gold for double-bond hydrogenation are measurable but extremely low (5). As a last step in this argument, the rates may be plotted directly against the heat of adsorption of hydrogen (Figure 6). All the reliable points lie on a smooth curve constituting the right-hand branch of a Volcano Curve; the result for copper is somewhat uncertain, but this metal is probably the sole resident on the steep left-hand branch of the curve.

It is legitimate but premature to ask why strengths of adsorption decrease with increasing Periodic Group number. One very simple answer has been given above for the case of oxygen. With carbon monoxide the situation is much more complex than has

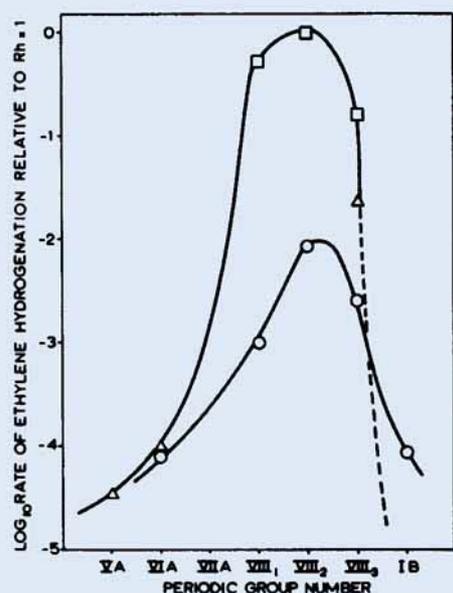


Fig. 5 Rate of ethylene hydrogenation on various metals relative to Rh = 1 as a function of Periodic Group number.

○ First row metals,
 □ second row metals,
 △ third row metals

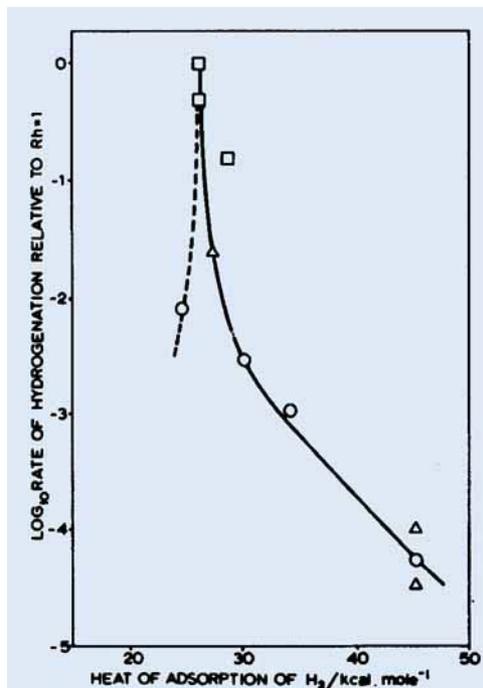


Fig. 6 Rate of ethylene hydrogenation on various metals relative to Rh = 1 as a function of the initial heat of adsorption of hydrogen.

○ First row metals,
 □ second row metals,
 △ third row metals

been suggested thus far. On many metals to the left of Group VIII, and on iron, the molecule dissociates into carbon and oxygen atoms even at room temperature, and these are now believed to be the initial species in the Fischer-Tropsch synthesis. When the molecule remains undissociated, as on palladium, reaction with hydrogen gives low molecular weight oxygenated products. The story of the two-dimensional chemistry of metal surfaces is still being written, but the principles on which it is based are now quite clear.

The Partial Transmutation of Catalytic Properties

It must by now be evident that the chemisorptive and catalytic properties of metals are inherent features of their chemistry which can

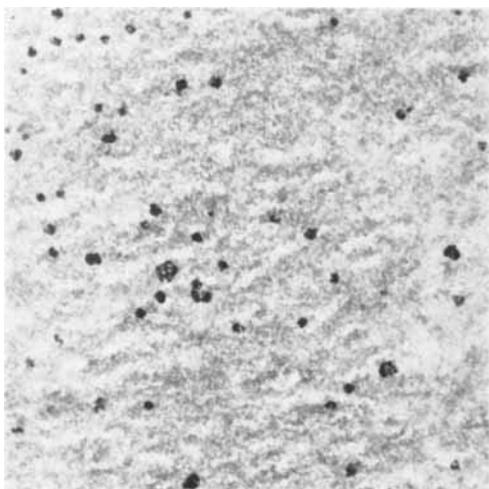


Fig. 7 Transmission electron micrograph of a 5 per cent palladium-silver alloy on silica (Pd = 63.5 per cent, Ag = 36.5 per cent). Magnification 50,000; 1 mm = 200Å. Individual particles are about 200Å in size

(Photograph by courtesy of Johnson Matthey Research Centre)

no more be imitated than lead can be alchemically changed into gold. That is not to say however that there is nothing to be done. It is a very old procedure to subdivide a catalytic metal into the smallest possible particles in order to optimise the fraction of atoms at the surface (6). By extremely simple chemical procedures it is easy to prepare very small metal particles (less than 100Å in size) on the surface of supports such as activated carbon, alumina or silica. As an example of the advantage to be gained by increasing dispersion, particles of 100Å have about 10 per cent of their atoms on the surface, whereas particles of 15Å in size (each having about 100 atoms) have 66 per cent of their atoms on the surface. A transmission electron micrograph of a somewhat less well dispersed catalyst (a 5 per cent palladium-silver alloy on silica) is shown in Figure 7: individual particles, many of which are in small aggregates, have sizes of about 200Å. Particular interest attaches to even smaller particles such as may be stabilised within the cages of zeolites: these may consist of half-a-dozen or so atoms, and such

particles of platinum (7) or rhodium (8) appear to be electron-deficient in comparison with bulk metal, and hence to assume some of the characteristics of the element next to the left in the Periodic Table. Very highly dispersed palladium has been formed on silica using divalent chromium ions adsorbed on the silica as reductant (9). This form of palladium is very much more active for ethane hydrolysis than larger particles, and hence it has become somewhat like rhodium. The hydrogenation activity shown by supported gold is thought to be due to extremely small particles which have not been detected, and there is evidence that gold in this state becomes rather like platinum (10). It seems likely that this will continue to be a stimulating field for research, in view of the possibilities it offers to improve and control the catalytic activities of the platinum metals.

One final example of partial transmutation may be given. Much research has been devoted to the binary alloys of nickel with copper, and of palladium with silver or gold, and to many other systems. Some of these find very important industrial uses. At least with the more straightforward alloys it is now clear that complete loss of identity of the components does not occur, but rather that each component gently and sometimes favourably modifies the properties of the other. Thus several cases are known where the specific activity of palladium is actually increased by the presence of an inert partner such as gold. This must be due to a partial transfer of electrons from gold to palladium with consequent benefit to its catalytic activity. Similar effects probably result from the use of selective poisons: thus electro-negative elements such as chlorine and sulphur, which find practical use in several applications, will donate electrons to the metal, while electropositive elements such as sodium or potassium will withdraw them. This is another active area for research where considerable advances may be expected.

Earlier in this paper the reader's attention was focused on a comparison of the properties

of sodium and of gold, the least and the most noble of metals. Gold has too many electrons to be a good catalyst, and it clings to them: rhodium, palladium and platinum have about the right number, but ruthenium needs more. Sodium loses its valence electron easily. Perhaps it is not too fanciful to imagine that by suitably combining pairs of metals of greater and lesser nobility it may be possible to synthesise alloys having just the optimum electronic structure required for the efficient

catalysis of a given reaction. But perhaps we may feel that it is a waste of effort to try to improve on what is already so good, and agree with Shakespeare when he said:

“To gild refined gold, to paint the lily,
To throw a perfume on the violet,
To smooth the ice, or add another hue
Unto the rainbow, or with taper-light
To seek the beauteous eye of heaven to
garnish,
Is wasteful and ridiculous excess.”

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Platinum Drug Receives Governmental Approval for Anti-Tumour Applications

The platinum co-ordination complex $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$ was first shown to have potent activity against animal cancers in 1969 by Professor Barnett Rosenberg and Loretta Van Camp at Michigan State University. After many years of toxicological evaluation and human clinical trials this compound has now received official approval as a drug by the U.S. Food and Drug Association (December 1978) and the U.K. Department of Health and Social Security (March 1979). The drug is marketed by the Bristol Myers Company under the name of Platinol in the U.S.A. and Neoplatin in the U.K. It has been specifically approved for chemotherapy of testicular and ovarian cancers although trials on other tumours are proving promising in the clinic. Similar approvals are being sought in nineteen other countries at the present time.

The Johnson Matthey Group and Rustenburg Platinum Mines have played an active role in the development of this drug which is likely to be the first of a new class of anti-

tumour agent. Professor Rosenberg's work was supported by the two companies from the very beginning while much of the chemical characterisation, analytical and stability data necessary for governmental approval was generated at the Johnson Matthey Research Centre.

Production development work and quality control studies were carried out at Matthey Bishop Inc. in the U.S.A. which houses the only approved production facility for the pure bulk drug.

Many groups throughout the world are at present working to advance platinum chemotherapy by developing superior drugs and by obtaining a better understanding of their mode of action. Clinical trials on several new compounds are scheduled for 1979.

An article by Dr. Eve Wiltshaw, of the Royal Marsden Hospital, on the clinical development of $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$ will appear in the July issue of this journal.

M. J. C.