Alloy Films of the Platinum Metals as Model Catalysts for Research

PART II—CATALYTIC ACTIVITY PATTERNS

By R. L. Moss

Warren Spring Laboratory, Stevenage, Hertfordshire

The first part of this article described methods for the preparation and characterisation of evaporated alloy films containing one or more platinum metals. Their use in catalyst research has provided new examples of the variation of catalytic activity with alloy composition and the formation of unexpected reaction products. Various secondary factors which might be involved in determining the activity of alloy catalysts have also been demonstrated in recent work with alloy films.

We know that the performance of a catalyst in practical use depends on more parameters than the intrinsic catalytic properties of the active component. For example, an active catalytic metal may be dispersed over a support material to extend the effective area but much of this area can be lost again through sintering or poisoning. Also, the performance of the catalyst may be determined by mass and heat transfer limitations and the life by mechanical strength. Nevertheless, we are still interested in optimum specific activity and may have definite requirements with respect to causing selective reaction. Part of the effort devoted to understanding and improving upon the specific activity and selectivity exhibited by the pure metals has involved the study of alloys as catalysts. Some of the advantages of using alloy film catalysts for this work were outlined in the first part of this article (1) on film preparation and characterisation.

It is the purpose of this second part to report under two headings progress made in recent work with alloy films containing one or more of the platinum metals. The first aspect concerns the structural complications that can superimpose on any pattern of catalyst performance which it is proposed to correlate with apparent bulk or surface electronic properties. Then there follows a summary of present information on the variation of catalyst performance with alloy film composition and the ideas put forward to interpret these results.

Structural Effects

We are concerned under this heading with two related problems. Suppose that experiments with alloys of various compositions show that enhanced catalyst performance occurs at a certain composition, x per cent A in the binary alloy AB. Can we assume (if variables such as surface area, distribution over the support, etc., are held constant) that the enhanced performance can be reproduced in alloys prepared by other methods, providing the same alloy composition is always selected? Again, can we correlate the enhanced performance with some property of the alloy which apparently occurs at the composition x per cent A? Recent experiments with alloy films of platinum metals show what is involved in answering such questions.

Divergence of Surface and Bulk Composition

Some pairs of platinum metals exhibit wide miscibility gaps at the moderate temper-

atures encountered in catalyst operation. Structural information from X-ray diffraction of alloy films of Pd-Rh and Ru-Pt was presented in Part I (1), showing the ranges over which two phases co-existed. One or both of the phases might occur at the surfaces of the alloy crystallites depending on the conditions of alloy preparation. If the actual *surface* composition is unknown, considerable uncertainty must arise in attempts to correlate catalyst performance with properties of the alloy associated with a selected *bulk* composition, in these circumstances.

Even in alloys such as Pd-Au and Pd-Ag, where it is generally accepted that complete solutions are formed at all compositions, the surface may be enriched by one component. This is due to the fact that the surface will always tend to acquire the composition which has a minimum surface energy. Further, during the course of a catalytic reaction, the surface will also tend to be enriched by the alloy component which forms the strongest bonds with the adsorbed reactant molecules. Surface enrichment may continue under extreme conditions to the point where "de-alloying" can be observed by X-ray diffraction (2), e.g. by treating Pd-Ag films in oxygen.

Work function measurements have been used to follow the extent of surface enrichment when alloy films of Pd-Ag (3), Pt-Au (4) and Pt-Ru (5) were exposed to carbon monoxide. Results obtained under mild conditions (10^{-4} Torr CO at $100°C$ for 16 hours) are summarised in Table I, which also indicates whether moderately strong bonding
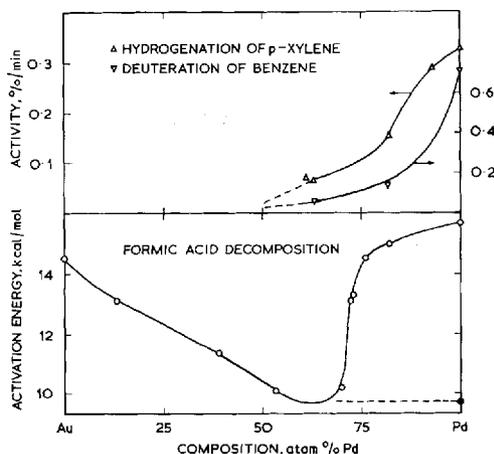

Fig. 1 *Activity patterns found using palladium-gold alloy films in the catalytic hydrogenation of para-xylene or deuteration of benzene (19) and in formic acid decomposition (6)*

would be expected, under these conditions, between the component metals and carbon monoxide. Clearly, where carbon monoxide could adsorb preferentially on one of the component metals in an alloy, then the surface was enriched by that component. The complications which this phenomenon imposes when interpreting catalysis by alloys are apparent.

Orientation Changes

The specificity of different crystal planes for gas adsorption and for catalysing reactions is well known for the pure metals. Such work is relevant to the "crystallite size" effect which is sometimes observed in supported metal catalysts. It is believed that the arrangement of surface metal atoms can vary with change of crystallite size, so that crystallites of different size may exhibit differences in specific activity or selectivity. Alloys of different composition (i.e. different proportions of A and B) may change with respect to crystallite orientation, again complicating the interpretation of catalyst performance.

A good example of the elucidation of this effect occurs in the work of Clarke and Rafter (6) on formic acid decomposition over Pd-Au alloy films, (Figure 1, lower part). The observed activation energy pattern is in

Table I

Surface Enrichment by CO Adsorption

Alloy	Expected CO Bonding		Effect on Surface	Refs
Pd–Ag	Pd(+)	Ag(—)	Pd enrichment	(3)
Pt–Au	Pt(+)	Au(—)	Pt enrichment	(4)
Pt–Ru	Pt(+)	Ru(+)	None	(5)

agreement in the Au-rich region with earlier results using Pd-Au alloy wires (7) but a marked deviation exists at the Pd-rich end. The texture of the films was shown to change markedly with composition, as explained in Part I (1). When pure Pd was prepared with a random orientation instead of a strong (111) texture, then the activation energy assumed a lower value (filled circle in Figure 1 lower part), in accordance with the results for Pd-rich wires.

Hydrogen Solubility

Alloys based on palladium, e.g. palladium-gold and palladium-silver, have been of considerable interest to research workers concerned with studying the effect of composition on catalytic and adsorptive properties (8, 9). Many alloy studies were prompted by the expectation that abrupt changes in these properties would occur once the d-band vacancies in palladium had been filled by alloying with the Group IB metal (see later). It has to be remembered, however, that palladium, and some of its alloys, have a remarkable capacity for hydrogen sorption. Hydrogen sorption may occur during catalyst preparation or during catalytic reaction from reactant hydrogen, hydrocarbons, etc. Once hydrogen has been dissolved in the uppermost surface layers of, say, Pd-Ag alloys, it may cause the alloys to behave electronically as if they had more than the nominal composition of silver present.

An example of the effect of hydrogen solubility is shown in Table II, which summarises some experiments with palladium-silver alloy films (10). Note first that the palladium-silver alloy with 11 per cent palladium is more active than the alloy with 96 per cent palladium, exhibiting a greater rate of carbon monoxide oxidation at a temperature approximately 100°C lower. When the alloy with 96 per cent palladium was heated in hydrogen at 250°C but cooled before pumping out the hydrogen, then the rate of carbon monoxide oxidation was increased. More effective hydrogen removal restored

		CO Oxidation Rate (Torr CO_2/min)			
			After Hydrogen at 250°C		
Alloy Composition	Reaction Temperature	As Prepared	Evacuated		
			0°C	250°C	
96% Pd– 4% Ag	238°C	0.35	0.67	0.29
11% Pd–89% Ag	142°C	2.60	2.09	—

Table II — Effect of Dissolved Hydrogen

the activity to its former value. In contrast, the alloy with 11 per cent palladium was not expected to dissolve hydrogen and correspondingly it did not show enhanced activity in comparable experiments. Although smaller in magnitude, the effect of dissolved hydrogen is in the same direction as the effect of dissolved silver in palladium.

A further example of the apparent involvement of hydrogen solubility in alloy catalyst behaviour is provided by experiments with palladium-rhodium films (Figure 2). In Figure 2 the alloy composition is expressed
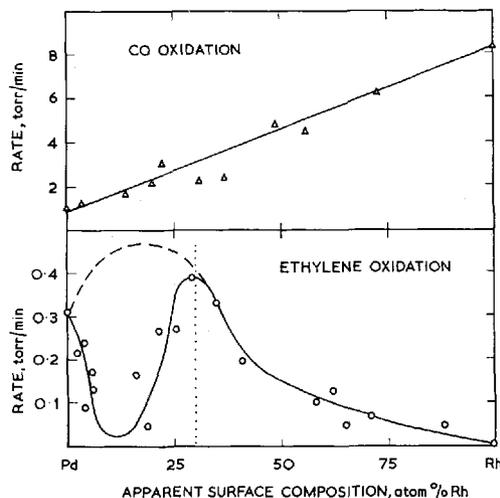

Fig. 2 Activity patterns found using palladium-rhodium alloy films in the catalytic oxidation of carbon monoxide (11) and ethylene (12). Vertical dotted line in lower part indicates composition limit for hydrogen solution in palladium-rich alloys

as "apparent surface composition", derived from X-ray diffraction measurements of the composition of one of the phases in this alloy and believed to exist at the crystallite surface. (This "correction" is not very significant for the present discussion.) The variation of activity with composition is simple for CO oxidation (11) where the catalyst had not been exposed to hydrogen in any way.

Consider now the lower part of Figure 2 which records rates of ethylene oxidation (12) where hydrogen from dissociated ethylene may dissolve in palladium-rich catalysts. Indeed, after catalytic reaction, alloys with up to 30 per cent rhodium showed evidence (13) of hydrogen solution (i.e. expanded lattices). Again, it would seem that a moderately simple activity pattern might have been observed, perhaps with a maximum near pure palladium. Instead, the pattern is complicated in the composition range 0 to 30 per cent rhodium where hydrogen solution is possible.

Activity Patterns and Interpretations

The widely different catalytic properties of metals such as palladium and gold have been explained in terms of the existence of the incompletely filled d-bands of the transition metals in Group VIII, as indicated by magnetic measurements. For some time it was believed that such measurements showed that palladium had about 0.6 d-band vacancies per atom. When filled by alloying with silver or gold, the observed abrupt changes in catalytic properties near the critical composition (60 per cent silver or gold) were apparently explicable. The "Electronic Factor" in catalysis was generally preferred to the "Geometric Factor" which came to be identified with lattice spacing and seemed unable to explain such substantial changes in catalytic behaviour.

Subsequent work on the electronic structure of palladium-silver and palladium-gold alloys involved various theoretical models to accommodate conflicting views on the number of d-band vacancies in palladium and how they are filled (see summary in (9)), e.g. at 38 ± 5 per cent silver (rigid-band model) or at 60 per cent silver (shifting band model). Again, in the charge-screening model the d-band is always filled on the silver atoms but only complete when there are sufficient silver atom neighbours to a given palladium atom. Thus both the number and geometrical arrangement of the component metal atoms become important for interpreting catalytic behaviour. A recent up-dating of the electronic factor in catalysis incorporated a treatment of the statistics of "surface ensembles" (14, 15).

In other work (16) emphasis is placed on the chemisorption properties of the *individual surface metal atoms*, moving away from the original interpretation of catalytic behaviour which rather emphasised the *collective electronic properties* of the bulk crystal. Chemisorption is treated as a localised phenomenon where the bond strength between the adsorbing atom and the surface atom is modified by neighbouring atoms. In a simple case, the surface might behave as an array of active palladium atoms in a diluent of silver atoms and no abrupt changes in catalytic activity with composition would be observed, but more complex activity patterns could be generated.

Recent papers concerned with adsorption on evaporated palladium-silver alloy films (13, 17, 18) have involved discussion in terms of the above ideas. Catalytic behaviour in four alloy systems, palladium-gold, palladium-silver, platinum-gold and palladium-rhodium, is outlined below.

Palladium-Gold

Work on the decomposition of formic acid (6) over palladium-gold alloy films (Figure 1, lower part) has already been mentioned with regard to the complication imposed by a change of crystallite orientation in palladium-rich alloys. Note the steady decrease in activation energy from pure gold to a minimum at 60 per cent palladium-40 per cent gold.
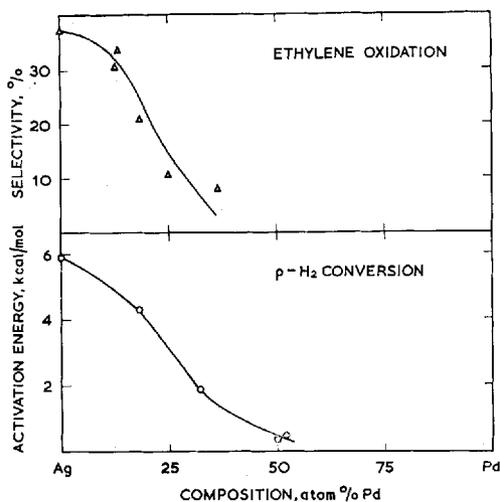
Fig. 3 *Activity patterns found using palladium-silver alloy films as catalysts for para-hydrogen conversion (20), or for the selective oxidation of ethylene (21)*

The upper part of Figure 1 shows that activity in two hydrogenation reactions (19) over palladium-gold alloy films falls from a maximum over pure palladium to low values at about 50 per cent palladium-50 per cent gold. Formerly, both these sets of data might have been confidently interpreted in terms of the simple *d*-band filling model. In contrast to the hydrogenating activity, the activity for benzene exchange with deuterium (19) persisted to very low palladium contents (not illustrated). This last result may relate to the more gradual manner in which the number of *d*-vacancy bearing surface sites will change with composition, expected when the *d*-band model is modified with regard to the occurrence of "surface ensembles".

Palladium-Silver

Para-hydrogen conversion (20) over palladium-silver alloy films (Figure 3, lower part), is characterised by very small activation energies for palladium-rich alloys, which begin to increase only when there is less than about 60 per cent palladium. It seems possible to have an explanation of the activity pattern on the basis of the simple band model when using this "ideal" catalytic reaction.

The selective oxidation of ethylene to ethylene oxide (21) over palladium-silver alloy films (Figure 3, upper part) decreased with palladium addition and became zero over alloys with more than 40 per cent palladium. The decrease was related to variation in the mode of oxygen chemisorption arising from changes in bulk electronic properties, i.e. change in the Fermi level.

Platinum-Gold

The reactions in a butane-hydrogen mixture (22) over platinum-gold alloy films above 300°C include the unusual formation of appreciable amounts of *n*-pentane, apparently by disproportionation, i.e. two C_4 molecules disproportionate into a C_3 and a C_5 molecule. Platinum, deactivated by cracking at 350–400°C, would also produce *n*-pentane and other products. A parallel was drawn between the platinum-gold alloy and the strongly poisoned platinum, viz., a surface with numerous inactive sites which are gold sites or carbon-covered platinum sites respectively. It seems that *isolation of active platinum sites* suppresses the cracking-isomerisation reaction but isolated sites can still catalyse the disproportionation.

Palladium-Rhodium

We are concerned in this system with catalytic behaviour over binary alloy films where both components are platinum metals. The oxidation of ethylene (12) exhibits a rather complex activity pattern (Figure 2, lower part), and the apparent involvement of hydrogen solution was discussed above. In the simpler test of carbon monoxide oxidation (11) (Figure 2, upper part), the activity pattern is a linear increase in rate with increase in the apparent rhodium content of the surface. We appear to have active rhodium atoms in a diluent of palladium.

Alloy Surface Sites

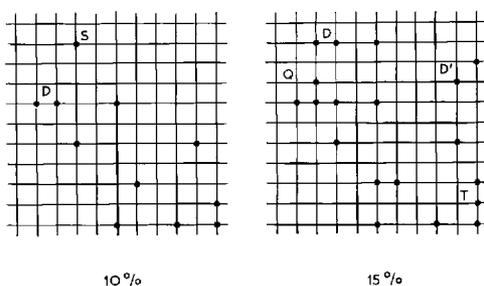The interpretation of alloy activity patterns (i.e. the variation of parameters describing

Fig. 4 *Square planar lattices occupied by A-atoms at intersections and 10 per cent (left-hand) or 15 per cent (right-hand) randomly substituted by B-atoms (black dots). Types of B-atom site are explained in the text*

catalyst performance with alloy composition) seems likely to involve more emphasis on the distribution of the component atoms on the alloy surface. Therefore it might be helpful to give an example of how the distribution of sites changes with composition.

Figure 4 shows square planar lattices, occupied by type A-atoms at the intersections, except where substituted by type B-atoms (the black dots). The left-hand diagram is part of a larger lattice, about 10 per cent randomly substituted by B-atoms, and contains isolated B-atoms (S) and isolated doublets (D). An isolated B-atom is defined here as having no B-atom neighbours on any of the four nearest lattice positions (i.e. positions marked "1" in the inset on Figure 5; B-atom neighbours at position "2" are permitted).

In Figure 4, right-hand diagram, about 15 per cent B-atoms have been randomly substituted for the original A-atoms. Now, there are present isolated doublets of two types, D and D' with different spacings (D' might also be regarded as two isolated atoms), an isolated (linear) triplet (T) and a T-shaped grouping of four B-atoms (Q). Further random addition of B-atoms soon diminishes the numbers of isolated sites containing various arrangements of small numbers of B-atoms. Figure 5 shows that the variation of isolated single B-atom sites with alloy composition passes through a maximum at 20 per cent B. The position of the maximum can be shifted to a lower composition by not permitting B-atom neighbours at lattice position "2" in the definition of an isolated single B-site. The B-doublet maximum is smaller and occurs at a higher composition. Conversely large unsubstituted groups of A-atoms soon become scarce with modest additions of B-atoms.

In conclusion, the use of alloy films has provided new activity patterns for interpretation at a time when there is renewed debate about the electronic properties of alloys and their surfaces and the correlation with catalytic behaviour. It is necessary to be aware of the complications imposed by structural and other effects on these patterns and some have been highlighted by recent experiments with alloy films of the platinum metals.
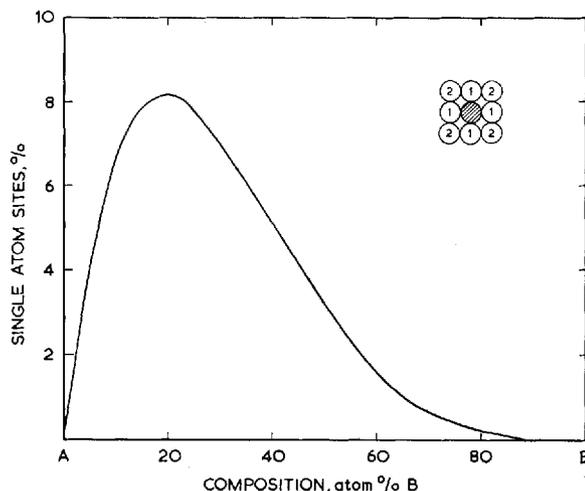

Fig. 5 *Variation of isolated single B-atom sites as a function of alloy composition. Inset: central (shaded) atom should have no neighbours at position 1, but may have neighbours at position 2*

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Potential Uses of Ruthenium-Molybdenum and Ruthenium-Tungsten Alloys

It has frequently occurred that basic work on an alloy system has been undertaken with one particular technology in mind but that progress has eventually taken place on an entirely different front. Such appears again to be the case with the ruthenium-molybdenum and ruthenium-tungsten systems, both of which, among a number of other refraction noble metal systems, were studied closely (1) some ten or more years ago for possible use in nuclear reactor technology.

Interest in them has now been revived, and in a paper from Bell Laboratories, Murray Hill, New Jersey (2), William A. Royer and his associates report that while evaluating materials for superconducting properties they noticed that films of ruthenium-molybdenum and ruthenium-tungsten deposited on thin sapphire slabs did not dissolve in the standard etching solution. The group thereupon re-examined Mo_5Ru_3 and W_5Ru_3 and re-established that these refractory alloys are very hard and scratch resistant, make adhesive films and are moderately reflective.

These properties, together with their high melting points and good acid resistance, suggested that such alloys might be useful in electrical contacts, for example in relays operating in corrosive atmospheres. Other possible applications where a durable coating is required include various cutting edges, die surfaces, and also mirrors in instruments for measuring the degree of atmospheric pollution.

The Bell workers deposited their films by sputtering on to heated sapphire substrates at 400 to 700°C. The films were up to 10 μm thick and their crystal structure depended upon the temperature of the substrate during deposition. The Bell team also found that the temperature coefficients of resistivity of these alloys could be varied between negative, zero and positive according to the temperature of the sapphire substrate during deposition. For W_5Ru_3 values ranged from -100 to $+100$ p.p.m./°C between 25 and 600°C. Such control of the temperature coefficient is valuable for thin film integrated circuitry as it allows thin film resistors to compensate for temperature induced changes in other components of a circuit.

F. J. S.

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