

Alloy Films of the Platinum Metals as Model Catalysts for Research

PART I—PREPARATION AND CHARACTERISATION

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Model platinum metal alloy catalysts for research purposes are conveniently prepared as thin films by simultaneous evaporation of the component metals. These catalysts can be characterised in some detail with respect to structural features such as phase-separation, crystallite size and orientation. In addition to the measurement of bulk composition, which would usually be carried out, advances have recently been made in analysing the surface composition, which is of greater significance for the discussion of catalytic behaviour.

Although the metals make up the majority of the elements in the Periodic Table, only a few of them, and particularly the platinum metals, are really useful as catalysts in the pure metallic form. If these pure metals have approximately the correct electronic or structural properties, then it is tempting to suppose that still better catalysts can be found by alloying. There are a number of reports in the literature of "synergistic" effects when platinum metals are used in combination as catalysts. Activity for liquid-phase hydrogenation of nitrobenzene (1) was enhanced at certain compositions when reduced mixed oxide catalysts were employed: 25 at.% Ru-Pt, 25% Ru-Pd, 15% Ir-Pt and 25% Rh-Pd. In other hydrogenation reactions (2) over supported platinum-rhodium alloys, activity was enhanced at 20 to 40% Rh.

Again, laboratory catalyst research with the objective of describing the catalytic activity of metals has often involved experiments with alloys. The catalytic activity of the transition metals, especially in hydrogenation reactions, has been correlated in the past with the existence of partially filled *d* bands. Many alloy studies were prompted by the expecta-

tion that catalytic activity should change abruptly once these vacancies had been filled by alloying with a Group IB metal. Palladium-gold is an excellent system for such fundamental studies (3).

Now for many years metallic films deposited on glass by vacuum evaporation have been used in laboratories to study the catalytic properties of the *pure* metals (4). The more recent extension of the metal film technique to alloys has already developed our understanding of certain alloy catalysts. Some interesting alloy systems are subject to phase separation, which may develop first at the catalyst surface and confuse the interpretation of results. This problem and other structural aspects of alloy catalysts are reasonably amenable to investigation when evaporated alloy films are prepared. It is also apparent that alloy film preparation can form the basis of a technique for exploring or "screening" alloy systems as catalysts in a variety of reactions.

In this first article, methods for the preparation and characterisation of evaporated alloy films are discussed with special reference to alloys containing one or more platinum metals. In a subsequent article an account

will be given of recent research involving such alloy catalysts.

Alloy Film Preparation

Evaporated films of pure metals for research purposes are commonly prepared by heating a metal filament in vacuum to a temperature at which the metal vapour pressure is 10^{-3} to 10^{-2} torr; the metal vapour is condensed on the cooled surface of the glass reaction flask containing the filament. A comprehensive account of metal film preparation by vacuum evaporation has been given by Holland (5). The review by Klemperer (6) should also be consulted regarding film preparation in the context of adsorption and catalytic reaction studies. The preparation of alloy films has also been reviewed (7) but more specific information is provided here on methods that have been employed successfully to prepare alloy films containing platinum group metals.

There are two main methods for the preparation of evaporated alloy films:

- (a) The two metals are co-evaporated either from an alloy source or from separate sources containing the pure metal components. On deposition, the mixed metal vapour can be quenched-cooled or a heated substrate can be used to encourage atom mobility after condensation.
- (b) The two metals are deposited successively on the substrate and are then annealed in vacuum or in the presence of hydrogen.

In the following account of alloy film preparation, the method of co-evaporation (also called simultaneous evaporation) will be described. This method has usually been adopted in preparing alloy films for catalytic work. During film formation, even by co-evaporation, regions rich in one component may develop, perhaps as a consequence of preferential nucleation. So, although co-evaporation was used, it was also usual to have a heated substrate (say 400°C) and to anneal the films after deposition.

Values of $P/M^{\frac{1}{2}}$ at 1200°C

Ru	Rh	Pd
9.5×10^{-14}	1.1×10^{-10}	1.4×10^{-5}
Os	Ir	Pt
—	1.0×10^{-14}	6.7×10^{-11}
Cu	Ag	Au
4.3×10^{-4}	2.1×10^{-2}	1.3×10^{-3}

Experimental Arrangements

Evaporation from an alloy source involves some consideration of the relative vapour pressures of the component metals. Preferential evaporation of one metal with a substantially higher vapour pressure would leave the film enriched overall with that metal and perhaps stratified into layers of different composition. If film deposition is followed by a homogenising treatment (and the film composition is subsequently determined) a moderate degree of fractionation during evaporation may not be a disadvantage. A guide to the likelihood of preferential evaporation from an alloy source is derived from Raoult's Law, viz., the value of the quantity $P/M^{\frac{1}{2}}$ where P is the vapour pressure and M is the atomic weight. Values of $P/M^{\frac{1}{2}}$ are shown in the table for platinum group and Group IB metals, using vapour pressure data at 1200°C . Where values of $P/M^{\frac{1}{2}}$ are roughly equal, evaporation from the alloy source without much fractionation can be expected. Alloys prepared for catalytic studies by evaporation from alloy wires confirm the usefulness of this guide. Thus, the composition of palladium-gold films (8) was found to be the same as the wire source whereas a 30% Ag-Pd alloy wire yielded a 50% Ag-Pd film (9).

If separate metal sources are used (and either co-evaporated or evaporated successively), the types of source and their positioning inside the reaction flask need attention if a uniform composition over the area of the reaction vessel is to be achieved. Presumably for catalytic work the experimenter will want this result. Non-conformity of composition

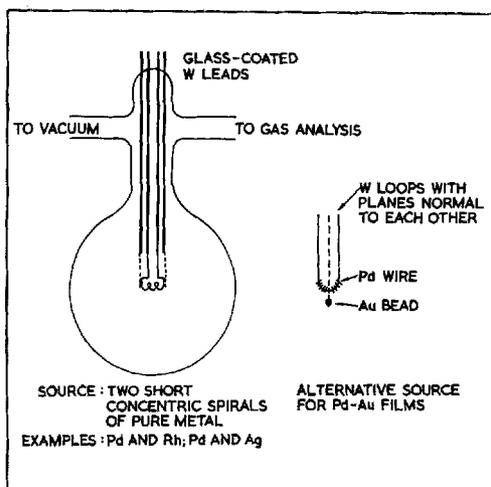


Fig. 1 Experimental vessel for alloy film preparation. Sources can be two spirals of the pure metals or alternatively pure metal beads or wire mounted on tungsten heating loops

can be exploited to advantage in some other types of surface study; for example, work function changes were measured in gold-platinum (10) and ruthenium-platinum (11) films at a number of positions along a composition gradient. Now a uniformly thick film should be deposited by evaporation from a bead of metal (on a tungsten heating loop) positioned at the centre of a reaction vessel made from a spherical-glass flask, or from a straight metal filament down the central axis of a cylindrical reaction vessel. However, the second metal source has to be designed and positioned about the first source with some care, if a uniform coating of the second component is to be achieved. The resulting binary alloy film should then exhibit a uniform composition over the reaction vessel surface.

A simple experimental arrangement for depositing alloy films is shown in Fig. 1 using separate metal sources which are short concentric spirals of 0.5 mm diameter wire. Rhodium-palladium (12) and silver-palladium (13) alloy films were prepared in this way; a spiral of alloy wire might be used, where appropriate (see discussion above). Spherical reaction vessels have also been used to prepare gold-palladium alloy films. (14, 15). Here the palladium source consisted of

10 cm of 0.2 mm palladium wire wound around the bottom of a 0.3 mm diameter tungsten hairpin. The gold source was a bead of gold formed on a tungsten hairpin and suspended about 2 mm below the palladium source. A cylindrical vessel has been used to prepare silver-palladium films (9) from alloy wire sources; a tungsten heating filament with a number of loops to absorb thermal expansion, and also to prevent the alloy beads formed during evaporation from running together, was placed down the axis.

With due regard to the lateral variation in (bulk) composition which can arise from changes in source geometry and positioning, it is desirable to analyse the alloy film at a number of representative points after use. A variety of methods for (bulk) composition analysis are convenient for this purpose, e.g. at the end of the measurements of catalyst activity/selectivity etc., the reaction vessel can be cut up and the composition of the film on a number of pieces determined by X-ray fluorescence analysis. Hence the mean (bulk) composition and the uniformity of composition is found.

Bulk Structure

At the temperature normally encountered in alloy film preparation and use in laboratory catalytic experiments, say up to 450°C, many pairs of metallic elements will not provide stable homogeneous alloys. However, gold-palladium and silver-palladium alloys, which have large negative enthalpies of formation, can be expected to exist as homogeneous solid solutions over the whole composition range. These alloys also provide the simplest systems for studying the effects of electronic structure in chemisorption and catalysis. While methods of surface composition analysis are still being developed (see below), presumably the experimenter will want to prepare such alloys with good bulk homogeneity and to demonstrate this fact. In these circumstances there would appear to be a little more justification for assuming that the surface and bulk compositions are equal. Alloy films of

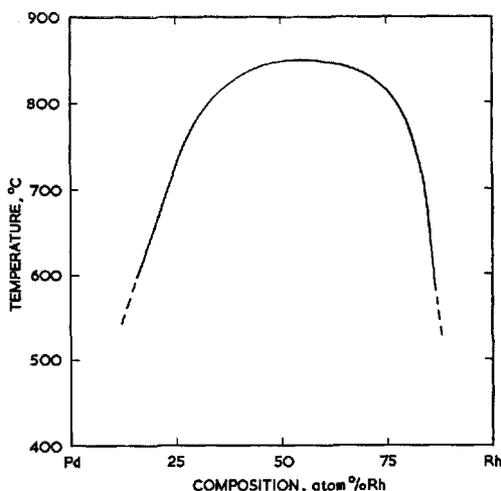


Fig. 2 Limits of the miscibility gap in the Pd-Rh system calculated from the lattice constants of the two-phase alloys between 600 and 825°C (see reference 16)

reasonable thickness will provide X-ray diffraction patterns and evidence of bulk homogeneity is provided by correct lattice constants and the symmetry of the X-ray line profile.

Some pairs of platinum metals exhibit wide miscibility gaps at lower temperatures. Examples (16) with the critical temperature of the miscibility gap in °C are: rhodium-palladium (830), iridium-palladium (1476) and iridium-platinum (975). The preparation of alloy films from such metal pairs raises some questions about the best tactics to employ. One alternative might be to prepare them as metastable solid solutions by vapour-quenching. Here the component metals are co-evaporated on to a very cold substrate to eliminate atom mobility on arrival and, because the vapour phase has no miscibility restrictions, the condensing atoms should be randomly distributed. To date, however, alloy films of platinum metal pairs have been annealed to encourage equilibration, e.g. at 400° or 600°C for rhodium-palladium (12, 17) and ruthenium-platinum films (11) respectively.

Figure 2 shows the limits of the miscibility gap in the rhodium-palladium system (16), predicting limited mutual solubility when

alloy films are equilibrated at 400°C. When rhodium-palladium films were examined by X-ray diffraction (after catalytic experiments at 240°C), the X-ray line profiles were asymmetrical in shape at compositions from 33 per cent rhodium to 91 per cent rhodium (17). Lattice constants could be calculated from the double diffraction peaks observed in films containing more than 56 per cent rhodium (up to ~90 per cent). (Fig. 3).

The structure of the catalytically-interesting ruthenium-platinum system has also been studied using alloy films (11). X-ray data are shown in Fig. 4, recorded in terms of the lattice spacing, d_{111} for platinum (face-centered cubic) and d_{002} for ruthenium (hexagonal). In the range 30 to 50 atomic per cent platinum, two phases were clearly visible, after equilibration at 600°C.

Electron microscopy/diffraction can also be applied to alloy films to provide information on crystallite aggregation, orientation and shape. When investigating the variation of catalyst performance with alloy composition, it is helpful to know how these features of film structure are also responding to the changing composition. Transmission electron micrographs are prepared from specimens of

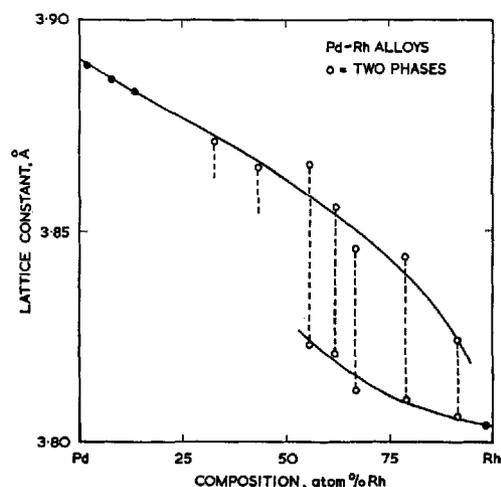


Fig. 3 Lattice constants for Pd-Rh alloy films, annealed at 400°C and used in catalytic experiments (reference 17). Broken vertical line joins values from double diffraction peaks and shows the limited mutual solubility

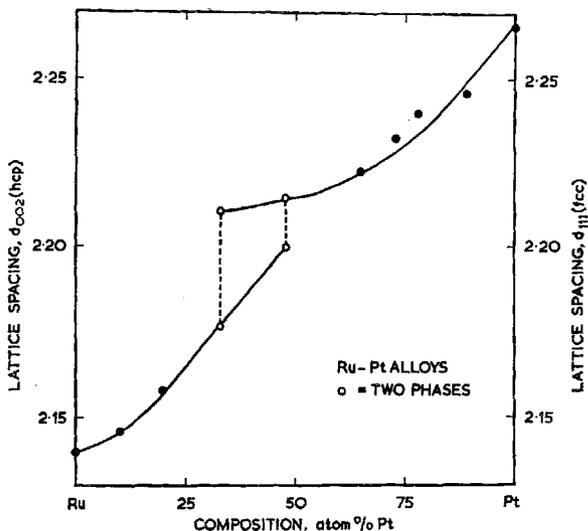


Fig. 4 X-ray data obtained from Pt-Ru alloy films, equilibrated at 600°C (reference 11). In the range 30 to 50 at. % Pt two phases were clearly visible

film stripped from fragments of the reaction vessel after catalytic measurements have been made. A good example of information from electron microscopy/diffraction found valuable in discussing catalytic results occurs in work on formic acid decomposition over annealed palladium-gold films (14). Pure palladium and palladium-rich films had a (111) texture whereas pure gold and gold-rich films had a (110) texture; marked changes in kinetic parameters resulted from preparing randomly orientated palladium films.

A subsequent article will go more fully into the subject of how various aspects of alloy structure, e.g. phase-separation or crystallite orientation, superimpose complications on patterns of catalytic activity which might be related to the alloy's electronic properties.

Surface Examination

Undoubtedly, in attempts to unravel the complicated behaviour of alloy catalysts, it would be a great help to know the *surface* composition of the alloy under investigation as distinct from its *bulk* composition. (By "surface composition" is meant the composition of the uppermost few layers of atoms.)

Even if phase-separation is not expected, the surface will tend to acquire the composition which has a minimum surface energy. So far, very few attempts have been made to probe the surface composition of alloys in any form used in catalytic work. Two methods used with alloy films are (i) work function measurements and (ii) Auger electron spectroscopy.

Work Function Measurements

Figure 5 shows the variation of work function with composition for two series of alloy films, gold-platinum (10) and ruthenium-platinum (11). After annealing at 300°C, co-evaporated platinum-gold films containing 15 to 88 per cent platinum had almost the same work function, 5.34–5.38 eV, equal or just lower than the value for pure gold (5.38 eV). Now the gold-platinum system exhibits a large miscibility gap and these results were interpreted as showing that, within its limits, the alloys prepared had a constant surface composition corresponding

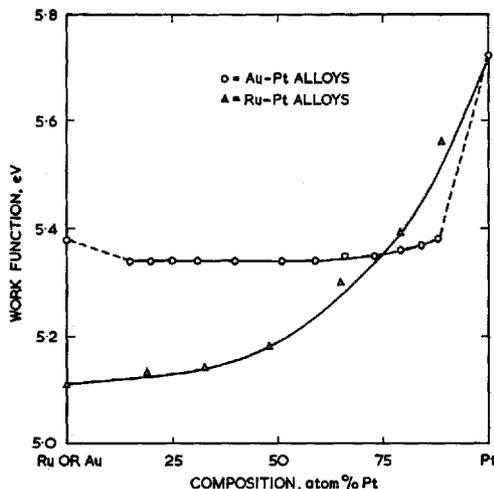


Fig. 5 Work function measurements on Au-Pt films after sintering at 300°C (reference 10) and Ru-Pt films, annealed at 600°C (reference 11). Results indicate that surface composition is constant over much of the Au-Pt (bulk) composition range but continuously variable in Ru-Pt films

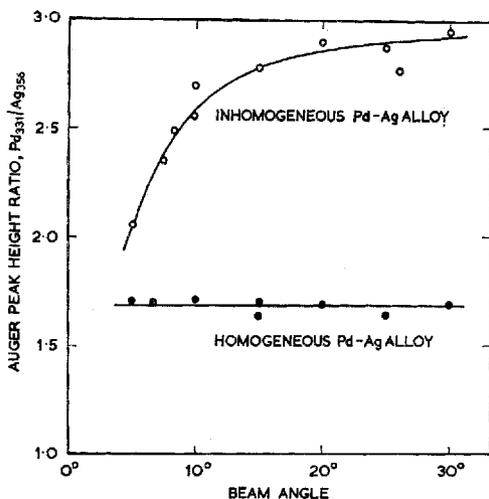


Fig. 6 Surface analyses can be made by Auger electron spectroscopy. The depth of sampling varies with change in the angle between the surface and primary electron beam (10° angle $\equiv 5\text{\AA}$). An inhomogeneous Pd-Ag film shows silver enrichment of the uppermost surface (reference 18)

to the gold-rich phase. In contrast, the apparent surface composition of ruthenium-platinum alloy films changes continuously with variation in bulk composition. The existence of a miscibility gap was mentioned above, and the surface may consist of more than one phase.

Auger Electron Spectroscopy

This promising technique is a consequence of the very limited escape depth of the Auger electrons excited by the electron beam incident on the sample. Palladium and silver show intense transitions at 331 and 356 eV respectively (18) and the surface composition of silver-palladium films was determined from these Auger peaks. The surface composition of silver-palladium films, carefully annealed at temperatures up to 400°C , was found to be a linear function of bulk composition.

If the surface has been enriched by one component, then the ratio of the peak heights of the Auger electrons from the two components should change with variation in the angle between the surface and the direction of the primary electron beam. As this angle decreases, the fraction of Auger electrons

originating from the uppermost surface increases. The lower curve in Fig. 6 was obtained from a well-homogenised silver-palladium film. The upper curve, from an insufficiently-annealed sample, shows silver enrichment of the uppermost surface, i.e. a lower ratio of palladium to silver peak height at small angles. At a 10° angle, information was being obtained from a depth of 5\AA .

In conclusion, methods for the preparation of alloys in thin film form are now well-established, together with the techniques needed to characterise these films with regard to bulk structure and surface composition. Alloys involving one or more of the platinum metals have been used in much of this work. It is therefore becoming possible, as will be shown in a subsequent article, to have a more complete discussion of the behaviour of alloys as catalysts.

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