JOURNAL OF CATALYSIS 26, 63–69 (1972)

Photoelectric Investigation of the Surface Composition of Equilibrated Pt–Ru Alloy Films in Ultrahigh Vacuum and in the Presence of CO*

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Received September 13, 1971

Photoelectric emission was studied from films of platinum, ruthenium, and their alloys, prepared by evaporating the metals onto a sliding quartz support. After annealing the initially multistratified films at 875 K and 7×10^{-8} N m^{-2} for 16 hr, they appeared equilibrated. The work functions of the alloys were found to be within the interval given by the work function of pure platinum (5.71 eV) and ruthenium (5.11 eV), respectively. Also the photoelectric emission constants varied regularly with composition. X-Ray diffraction data confirmed the presence of a miscibility gap; at least two phases coexist for films containing 30–50 at % Pt. The increase in work function caused by adsorbed carbon monoxide also varied regularly with composition, reaching its highest value for ruthenium. No chemisorption-induced surface aggregation of one alloy component, as previously found for Ag–Pd + CO and Au–Pt + CO was detectable for Pt–Ru + CO. It is concluded that most Pt–Ru films contain more than one alloy phase in their surfaces.

I. INTRODUCTION

Numerous reactions of hydrocarbons, in particular hydrogenations, are efficiently catalyzed by transition metals. Among them, platinum, palladium, and rhodium are very active but ruthenium is a relatively poor catalyst for most hydrogenation reactions. It is therefore remarkable that, in specific cases, alloys of platinum and ruthenium exhibit a catalytic activity exceeding that of platinum (*1–12*).

Up to the present, the reason for this apparent synergism has not been clarified. We, therefore, concluded that it would be desirable to study first the surface composition of these alloys, as there are now numerous data for other alloy systems (*13–17*), which prove that the surface composition often differs markedly from that of the bulk and as it has been found that the composition of the surface can be changed due to selective chemisorption (*16*, *17*). We have studied the Pt–Ru system with the methods which have proved successful for other alloys. For this purpose, thin films prepared in ultrahigh vacuum are preferred because equilibration can be achieved at lower temperatures than with bulk samples (e.g., foils). This is of particular importance for Pt–Ru alloys which due to the high heat of sublimation of either metal are expected to equilibrate at relatively high temperatures (*18*). The photoelectron emission of the equilibrated films has been studied before and after gas adsorption and from these data the work function and the surface potential were derived. The latter parameter was used for "surface titration." CO has been used to estimate the surface composition of the

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* This work is part of the thesis "Electron emission, surface composition and adsorption phenomena of metals and alloys: Photoelectric emission of clean and CO covered films of Au–Pt, Ag–Pd and Pt–Ru alloys and their components." by R. Bouwman, Leiden Univ., 1970.

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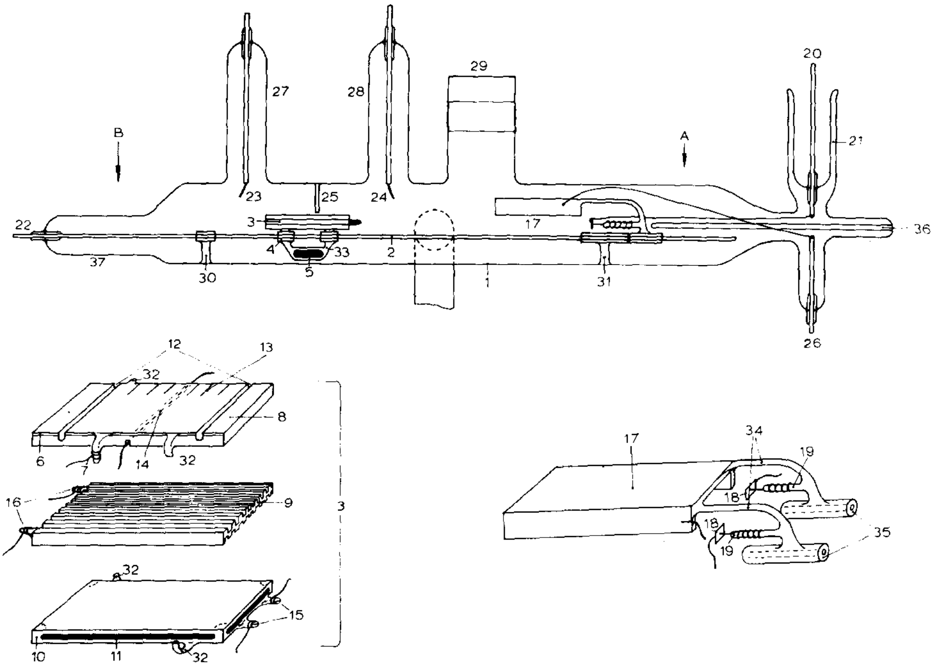

FIGURE 1

alloys because of its nondissociative character and because of the large difference in the change of the work function of Pt and Ru caused by CO-adsorption (*19*, *20*).

Attention was focused not only on the surface composition of the equilibrated films which cannot be predicted by existing theories, but also on the possible changes of this composition due to chemisorption. This "chemisorption-induced surface aggregation" has been discovered previously for the systems Au–Pt + CO (*16*) and Ag–Pd + CO (*17*), but from the theoretical concepts which were found valid for these systems it seemed unlikely that such phenomena should occur to a large extent for Pt–Ru. This system can, therefore, serve as a test of these ideas.

II. EXPERIMENTAL METHODS

General experimental techniques including ultrahigh vacuum, metal deposition, alloy analysis, etc., have been described elsewhere (*16*, *19*, *20*). A serious problem inherent to the lattice energy of Pt and Ru is the relatively high temperature which is expected to be necessary for equilibration of alloys of these metals. On the basis of previous results on the equilibration of thin metal and alloy films (*18*), the Pt–Ru alloy films can be expected to equilibrate at about 800–900 K. Because Pyrex supports are no longer mechanically stable at these temperatures, a different type of phototube to that used in previous work, is required. The tube which permits annealing of the film up to 1000 K is shown in Fig. 1. It comprises a Pyrex housing (1) having a diameter of 50 mm. Though one end, two elongated parallel tungsten rods (2) are fused (these are shown as one in Fig. 1). A quartz photocathode assembly (3), shown in detail, sliding over rods (2) on four small tubes (4) is provided with a Pyrex glass clad iron bar (5) to make magnetic operation possible from the outside. The surface of the cathode support is in electrical contact with the tungsten rods through a baked platinum paste* strip (6), fused platinum wire (7) and platinum tubes, fused within the Pyrex sliding tubes (4).

The cathode carrier consists of quartz

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* Platinum paste N758 (Johnson, Matthey & Co., Ltd., London)

cathode support (8), quartz oven element (9) containing wound tantalum wire (ϕ 0.15 mm) and a baking plate assembly comprising two quartz slabs (10) and sandwiched platinum foil (11). The cathode support (8) is provided with two slots (12), calibration marks (13) and a slot for a thermocouple (14). The latter consists of stretched Pt/Pt–10% Rh wire (ϕ 0.25 mm) enveloped by a quartz capillary (not shown). The terminals of the thermocouple are connected with "bumpers" (15) made of the corresponding thermocouple materials.

The terminals of the oven element are secured over two small quartz rods (16) and connected to the respective platinum tubes within sliding tubes (4), in order to make electrical contact with the tungsten rods (2) possible. The thermocouple terminals (15) are brought into electrical contact with the outside by moving the cathode assembly into a heat reflector shield (17) where it contacts deadends (18) made of Pt and Pt–10% Rh, respectively, and mounted on flexible tungsten springs (19) (ϕ 0.20 mm). The deadends are respectively connected to fused tungsten leads (20) by Pt and Pt–10% Rh wires. The tungsten rods which are fused through a small Dewar (21) can be cooled with melting ice to form a cold reference junction. (In Fig. 1, the Dewar part has been rotated over an angle of 90° around the main axis of the phototube.)

The quartz/tantalum oven element is brought to incandescence by applying a voltage (80–150 V) at outparts (22). A heat shield (17) consisting of Pt-foil stretched around a quartz skeleton protects the surrounding Pyrex housing against heat radiation. Metal evaporation sources (23, 24) are situated on either side of a glass screen (25), the latter having a double function:

1. It prevents the sources from "seeing" each other.
2. It is used to protect both terminal zones of the photocathode during deposition of the metals in order to obtain zones of the pure metal on the extremities of the cathode carrier and an intermediate alloy gradient, slots (12) acting as barriers for lateral diffusion from the alloys across the surface and towards the pure metal zones.

The platinum shield functions as collecting anode and is connected with anode output (26).

After severe predegassing at 1000 K, the films can be sintered at 900 K while maintaining a vacuum of less than 7.10^{-8} N m^{-2}*.

The bimetal film is prepared by alternately moving the cathode assembly between a position near to source (23) and near to source (24), thereby obtaining a multistratified bimetal film system, generally consisting of 16 alternating layers of Pt and Ru having a total thickness of 25–50 nm and 100 nm near the edges of the photocathode. This means that each individual pure metal layer has a thickness of about 10 atomic layers. X-Ray diffraction data from these films indicate complete alloying. Immediately after preparation of the film, eight positions (corresponding with the calibration marks) were investigated. These positions were again studied after equilibration at 875 K and after admission of CO (1.3×10^{-2} N m^{-2}) and after exposure to CO ($p = 1.3 \times 10^{-2}$ N m^{-2}) during 16 hr while heating the film at 373 and 473 K, respectively.

III. Results

Relevant results on the work function Φ and the emission constant M are compiled in Tables 1 and 2.

Figure 2 shows that immediately after preparation of the film by sublimation on the noncooled quartz cathode support, the work function rises from Ru to Pt.

In this case, Pt was evaporated last which is shown by the high values of Φ, particularly in the range 60–100 at % Pt. This curve is broken in Fig. 2, because it reflects only an arbitrary state of the film characterized by a coarsely known set of evaporation conditions. It is beyond doubt that in this stage, the film is far from equilibrium. After sintering during 16 hr at 875 K, all values of the work function have changed and appear to be lying be-

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* 1 N m^{-2} = $7.501.10^{-3}$ Torr.

TABLE 1

THE WORK FUNCTION Φ(eV) AS A FUNCTION OF THE OVERALL COMPOSITION FOR CLEAN AND CO-COVERED Pt–Ru FILMS

x(at % Pt)[a]	Φ_{fresh}	Φ_{eq}	$(\text{CO})_{293\text{ K}}$	$\Delta\Phi$	$(\text{CO})_{373\text{ K}}$	$(\text{CO})_{473\text{ K}}$
0	5.08	5.11	5.71	0.60	5.70	5.70
19	5.40	5.13	5.69	0.56	5.69	5.68
33	5.55	5.14	5.66	0.52	5.64	5.66
48	5.62	5.18	5.64	0.46	5.66	5.65
65	5.69	5.30	5.55	0.25	5.55	5.55
79	5.68	5.39	5.55	0.16	5.55	5.54
89	5.72	5.56	5.65	0.09	5.66	5.66
100	5.69	5.71	5.75	0.04	5.74	5.75

[a] The values of the bulk composition of the alloys are known with an accuracy of ±5 at %.

TABLE 2

THE EMISSION CONSTANT M $(\times 10^{-12})$(electrons photon^{-1} deg^{-2}) AS A FUNCTION OF THE OVERALL COMPOSITION FOR CLEAN AND CO-COVERED Pt–Ru FILMS

x(at % Pt)[a]	M_{fresh}	M_{eq}	$(\text{CO})_{293\text{ K}}$	$(\text{CO})_{373\text{ K}}$	$(\text{CO})_{473\text{ K}}$
0	12.8	6.0	2.8	2.7	2.7
19	15.3	5.8	2.9	2.8	2.7
33	20.1	6.4	3.8	4.1	4.0
48	19.2	6.9	5.6	5.8	5.5
65	23.6	7.5	6.4	6.2	6.1
79	23.2	7.5	7.2	7.0	6.9
89	26.2	8.9	8.8	8.4	8.5
100	28.0	9.8	10.0	10.2	9.8

[a] The values of the bulk composition of the alloys are known with an accuracy of ±5 at %.

tween those of pure platinum and pure ruthenium. Repeated annealing at 875 K did not cause appreciable change of the curve from which we conclude that the film was properly equilibrated. (These values were checked only briefly and have not been taken up in Tables I and II, which contain only the values representative of the equilibrated films after the last annealing cycle completing a total annealing period of 40 hrs.)

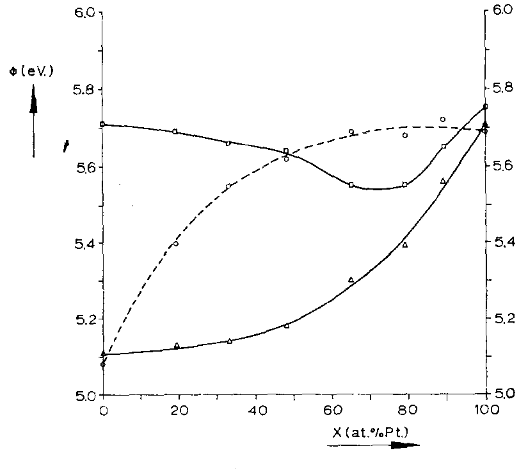

FIGURE 2

After admission of CO the work function of either metal and all alloys is raised. The change of the work function, $\Delta\Phi$, decreases monotonically from pure Ru to pure Pt (Fig. 3).

The behavior of the emission constant M before and after admission of CO is displayed in Fig. 4. In contrast with previous results on Au–Pt (*16*) and Ag–Pd (*17*) alloys, the M vs x curve does not display maxima or minima. The change in M brought about by CO chemisorption is most pronounced on Ru-rich samples and decreases with increasing Pt-content.

After 16 hr during which the film was kept in direct contact with CO at a pres-

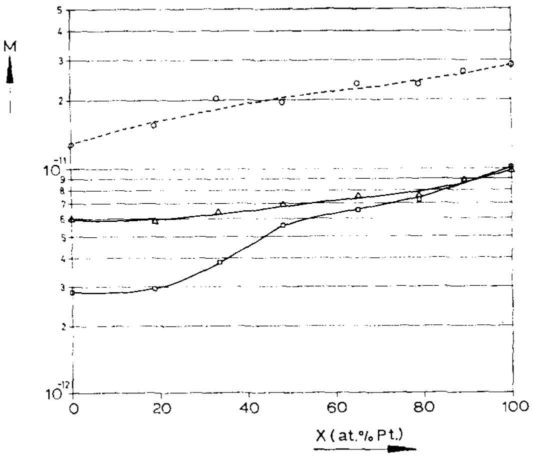

FIGURE 3

sure of 1.3×10^{-2} N m^{-2} at, respectively, 373 and 473 K, the work function of all alloys remains constant within 0.02 eV and the emission constant remains unaltered within 0.4×10^{-12} electrons $photon^{-1}$ deg^{-2}.

The X-ray diffraction data of the alloys are shown in Fig. 5. As Pt and Ru crystallize in different structures, we have plotted the spacing between the most closely packed crystal planes (d_{111} for Pt and d_{002} for Ru) versus the bulk composition to obtain an impression of the mutual solubility of the metals into each other's lattices.

The results suggest that less than 30 at % Pt is dissolved in the hexagonal Ru-lattice, while less than about 50 at % Ru can be incorporated into the fcc lattice of Pt. In the range 30–50 at % Pt, two phases are clearly visible. It is interesting to compare these data with X-ray diffraction data from Pt–Ru alloy powders (*21*) prepared according to the Adams method and which have been equilibrated at 748 K (Fig. 6). Although the shape of the curves is not the same as for our films, it is clear that phase separation occurs.

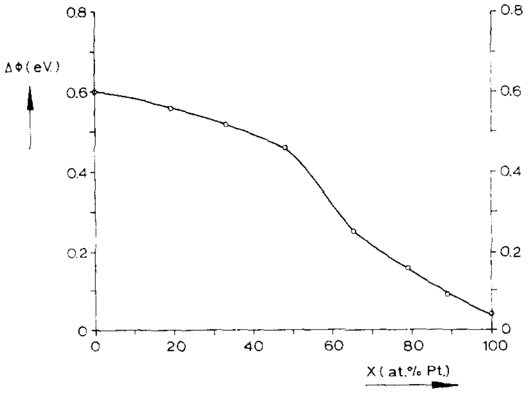

FIGURE 4

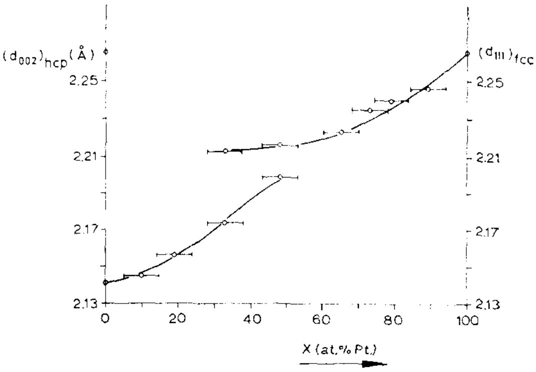

FIGURE 5

IV. DISCUSSION AND CONCLUSIONS

A number of conclusions can be made which may contribute to the problem of catalytic synergism. First it has been shown by means of X-ray diffraction both for thin films and for reduced powders, that a number of Pt–Ru compositions annealed at temperatures, which are relatively high with respect to catalysts used by other authors, consist of more than one phase. Our results on films indicate a miscibility gap between 30 and 50 at % Pt (Fig. 5). As in this range, crystallites of either phase are large enough to cause detectable X-ray lines, it is likely that the actual miscibility gap is even wider (Fig. 6).

These results are at variance with find-

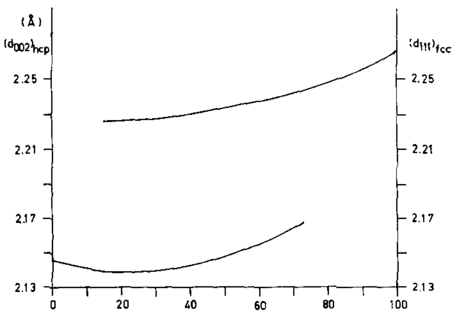

FIGURE 6

ings of McKee and Norton (*3*) who reported solubility of up to 65 at % Ru in Pt for alloys annealed at about 300°C, which they correlated with the only literature data available on the phase separation of Pt–Ru alloys published by Nemilov and Rudnitzky (*22*) and by Ageev and Kuznetsov (*23*), respectively. The latter authors studied the system after annealing at 1900 K and found complete solubility up to 80 at % Ru. However, as solubility increases with temperature, it can be safely said that the miscibility gap must be much wider at the lower temperatures used in our work and that of McKee and Norton. It appears possible that McKee's catalysts were metastable mixtures rather than two equilibrium phases.

Our results, especially those emanating from the surface titration, suggest that the apparent surface composition of these alloys changes gradually with that of the bulk. In this respect, the Pt–Ru system appears to differ from other two-phase alloys studied previously such as Cu–Ni and Au–Pt where one phase tends to surround the crystallites of the other phase. Consequently, the surface composition of the latter alloys remains constant for all compositions within the miscibility gap. In those systems, this peculiar arrangement could be interpreted: (a) kinetically in terms of the largely different surface diffusion properties of both elements; and (b) thermodynamically in terms of the larger difference in surface energy of the two phases.

The present finding that for Pt–Ru the surface composition does change with that of the bulk can be due to either of two possible causes:

1. The rate of surface diffusion of the two elements and the surface energies of the two coexisting alloys differ much less than in, e.g., the Cu–Ni system; consequently no enveloping of one phase by the other alloy takes place.

2. The phase diagram of the Pt–Ru system, which, to our knowledge, has never been studied systematically by modern methods exhibits more stable phases than only the two alloys suggested by Fig. 5. If three or more alloy phases occur, of which only combinations of two coexisting alloy phases may be present according to the equilibration model proposed previously (*13, 14*), it is clear that films of large different overall compositions must exhibit surfaces of different compositions.

The absence of chemisorption-induced aggregation of one alloy partner in the surface as encountered for the IB–VIII alloy systems studied so far, where chemisorbing CO enhances the group VIII element concentration in the surface, is easily explained by the chemical similarity of Pt and Ru. If both atoms form bonds of comparable strength with the chemisorbing molecule, there is evidently no driving force for preferential aggregation. The absence of this phenomenon for this system, therefore, is in agreement with our views on it.

The present results, although not leading to an unequivocal explanation of the high catalytic activity reported for Pt–Ru alloys, support speculations on a posssible cause for this phenomenon. As we saw above, our results suggest that more than one phase appears in the surface. This is quite unusual, as for the other alloys studied in the past in our laboratory, *only one phase* was responsible for adsorption catalysis and the energy barrier of electron emission. We therefore wonder whether some of the typical catalytic anomalies of the Pt–Ru system might be due to the grain boundaries in the catalytic surface when crystals of *two different alloy phases* are in contact with each other. This idea was brought forward (*15*) to explain the catalytic anomaly reported by Emmett and Gharpury for those Cu–Ni alloys where the enveloping phase becomes so thin that it is likely to break up into separate scales, exposing part of the kernel of the enveloped system. In that case, the catalyst anomalies were tentatively ascribed to contact lines in the surface of crystals of two coexisting alloys.

ACKNOWLEDGMENTS

The investigations were supported by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.) The authors are indebted to Mr. F. C. Kauffeld whose skill in constructing the phototube was essential for this work.

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