Mixed Platinum Metal Oxide Catalysts

ACTIVITY PATTERNS IN ALLOY SYSTEMS

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In a previous paper (1) we demonstrated that ruthenium-platinum oxides on reduction under mild conditions yielded catalysts whose activity was superior to that of reduced platinum oxide for a number of hydrogenation reactions. We have now extended our work to examine a range of mixed platinum metal oxide systems, particularly the iridium-platinum, palladium-platinum, rhodium-platinum, rhodium-palladium and ruthenium-palladium systems, and find that the phenomenon of an activity maximum at some point is one of wide occurrence. The mixed oxides were prepared by methods similar to that described previously for ruthenium-platinum oxides; salts used were ammonium chloroplatinate, palladium chloride, ruthenium trichloride, rhodium trichloride, and ammonium chloroiridate or iridium tetrachloride.

In Fig. 1 we plot the activity (measured in ml H_2 STP min^{-1} $(10\ mg)^{-1}$) of reduced ruthenium-palladium, iridium-platinum and rhodium-palladium oxides for the reduction of 6 per cent nitrobenzene in methanol at 30°C: our former results for reduced ruthenium-palladium oxides are included for comparison. We previously (1) advanced the hypothesis that the observed variations in activity are determined by the electronic constitution of the catalysts. This can be given quantitative expression in terms of the fractional number of d-electron vacancies per atom in each catalyst, assuming all to be homogeneous alloys, and we may now explore the applicability of this concept to our results. The fractions of d-electron vacancies per atom for the pure metals are taken to

be (2): Pt and Pd, 0.6; Rh, 1.4; Ir, 1.7; and Ru, 2.2: values for mixtures are obtained by linear interpolation.

In Table I we have listed the maximum rate observed with each alloy system and the composition at which this occurs (from Fig. 1). We then list the composition at which
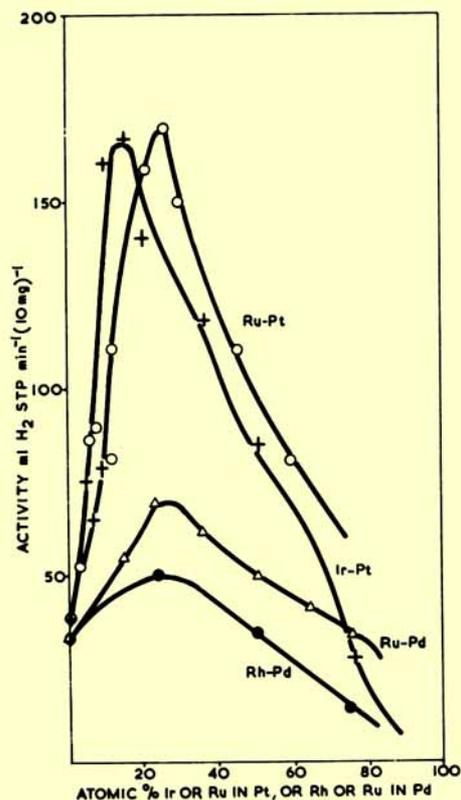

Fig. 1 The activity of reduced Ru-Pt, Ru-Pd, Ir-Pt and Rh-Pd oxides for the hydrogenation of 6 per cent nitrobenzene in methanol at 30°C

Table I				
Catalytic Activity for Nitrobenzene Hydrogenation and Electronic Structure of Ru-Pt, Ru-Pd, Ir-Pt and Rh-Pd Systems				
System	Maximum activity ml H_2 STP min.$^{-1}$ (10 mg)$^{-1}$	Composition at which activity is maximum	Composition for 1.0 electron hole/ atom	Composition for 0.75 electron hole/ atom
Ru-Pt	170	25 atom % Ru	25 atom % Ru	10 atom % Ru
Ru-Pd	70	25 atom % Ru	25 atom % Ru	10 atom % Ru
Ir-Pt	170	15 atom % Ir	36 atom % Ir	13.5 atom % Ir
Rh-Pd	50	25 atom % Rh	50 atom % Rh	18.5 atom % Rh

in each system there should theoretically be exactly 1.0 electron holes per atom. In two systems (Ru-Pt and Ru-Pd) this occurs precisely at the composition giving highest activity, but in the remaining systems the agreement is unsatisfactory. We have also evaluated the composition at which there should be 0.75 electron holes per atom and then find that in the Ir-Pt and Rh-Pd systems this composition tallies closely with that giving maximum activity.

These results lead us to the following generalisations:

(1) **To obtain the highest activities in nitrobenzene hydrogenation, Pt must be a component of the mixture;** in this sense Pd cannot replace Pt although both have nominally the same electronic structure.

(2) **When mixtures of metals from adjacent vertical groups are used, maximum rates of nitrobenzene hydrogenation occur when the electron hole/atom ratio is about 0.75; with metals from non-adjacent vertical groups, the optimum value of this ratio rises to about 1.0.** There are clearly other factors besides the electronic structure of the component metals determining the catalytic properties of alloys.

In our previous paper (1) we showed with Ru-Pt oxides that activity maxima were shown in a number of other hydrogenations, these maxima occurring at different compositions. Table II summarises the systems in which distinct activity maxima have been observed. We have not yet examined these reactions in sufficient detail to make it worthwhile recording the compositions (or electron hole/atom ratios) at which maximum rates occur, and no generalisations have yet emerged. In several cases however maximum rates in olefin hydrogenation occur at about the same compositions at which maximum rates of nitrobenzene hydrogenation are

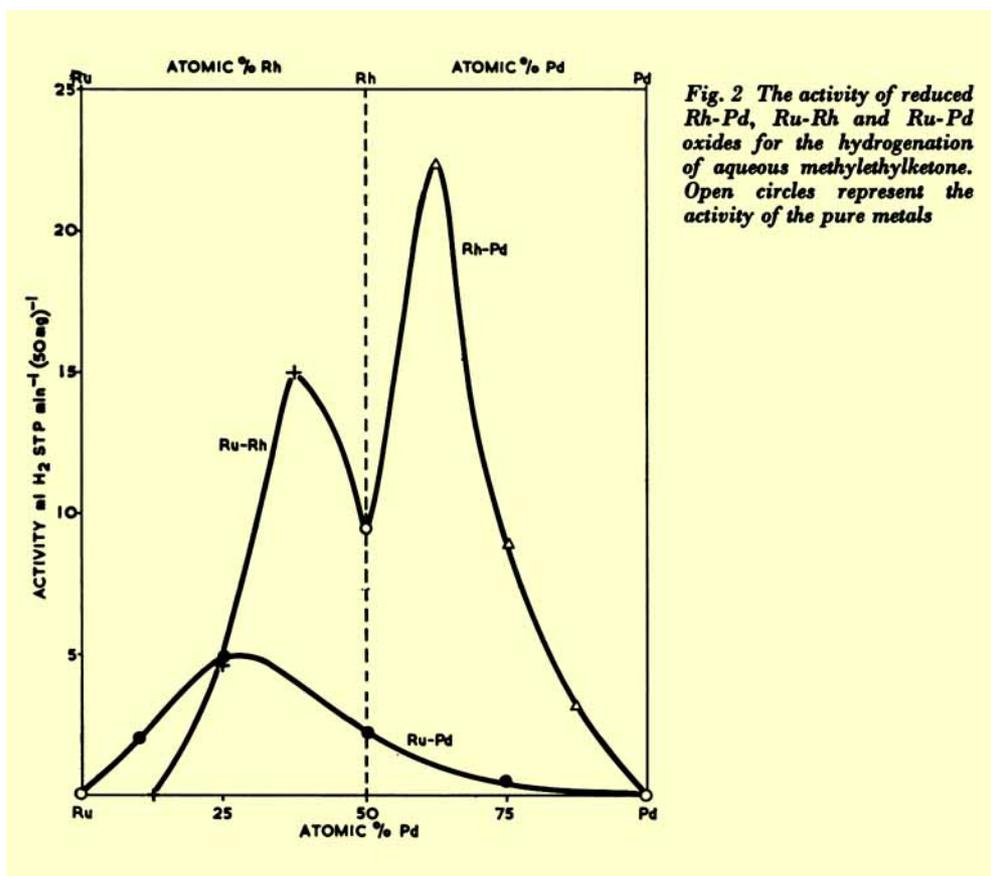| Table II		
Reactions and Catalyst Systems Showing Activity Maxima		
Reactant	Solvent	Catalyst Systems
Maleic acid	methanol	Pd-Ru, Pt-Ir, Pt-Ru
Cyclohexene	methanol	Pt-Ir, Pt-Ru
2-Methylbut-3-en-2-ol	methanol	Pd-Ru, Pt-Ir, Pt-Ru
Benzene, phenol	methanol, water	Pd-Rh, Pt-Rh
Methylethylketone	water	Rh-Ru, Pd-Rh, Pt-Ru

Fig. 2 *The activity of reduced Rh-Pd, Ru-Rh and Ru-Pd oxides for the hydrogenation of aqueous methylethylketone. Open circles represent the activity of the pure metals*

observed. A clear illustration of the lower activity of pure metals in comparison with their mixtures or alloys is shown in Fig. 2, where rates of hydrogenation of aqueous methylethylketone are plotted against atomic composition for the Rh-Pd and Ru-Rh systems.

However, the catalytic properties of a metal cannot be reproduced by compounding equi-atomic proportions of the metals lying to each side of it in the Periodic Classification: for example, the activity of the mixture of 50:50 Ru-Pd for hydrogenation of methylethylketone is much less than that of pure rhodium as can be clearly seen from the bottom curve of Fig. 2.

The final demonstration that the electronic structure of the catalyst is not the sole factor in deciding the positions at which

activity maxima occur comes from results we have obtained with reduced Pd-Pt oxides. Since both of these metals are taken to have 0.6 electron holes/atom, no activity maxima are to be expected on electronic grounds; nevertheless they are observed. The activities shown in Fig. 3 are relative to those of palladium and platinum separately: in the cases of the hydrogenation of 1-pentene and of nitrobenzene, the activities of both metals are essentially the same. Maxima for both these reactions occur at about 15 atomic per cent platinum. Also shown in this figure are results obtained by McKee and Norton (2) for the reactions of propane hydrogenolysis and of methane-deuterium exchange at 150°C over palladium-platinum alloys obtained by reduction of mixed salt solutions by sodium borohydride. In these cases the
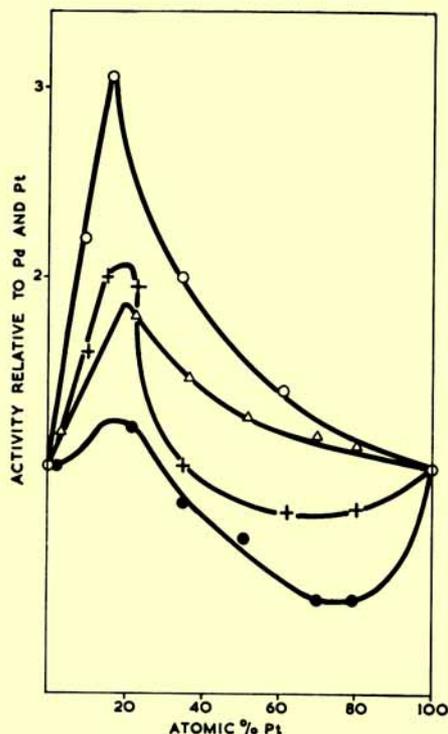
Fig. 3 *The activities of reduced Pd-Pt oxides for the hydrogenation of 1-pentene in methanol (○) and for the hydrogenation of nitrobenzene in methanol (+), and of Pd-Pt alloys for propane hydrogenolysis (△) and for methane-deuterium exchange (●)*

rates are relative to the rate expected if there were a linear relation between activity and atomic composition. In the case of propane hydrogenolysis, the maximum enhancement also occurs at about 15 atomic per cent platinum, although rates of methane exchange are generally less than predicted assuming additive behaviour of the two metals, a fact not explicitly commented on by McKee and Norton. The rate of hydrogenation of 2-methylbut-3-en-2-ol is a maximum at about 20 atomic per cent platinum, and we therefore conclude that this composition possesses some properties which maximise catalytic activity.

Although we cannot yet claim to have established a coherent body of satisfactory observations on our reduced oxide catalysts, far less to have understood their meaning fully, we nevertheless feel confident that we can, by continuing this line of investigation arrive, in due course, at some generalisations which should have considerable predictive value.

References

1 G. C. Bond and D. E. Webster, *Platinum Metals Rev.*, 1965, **9**, 12
2 D. W. McKee and F. J. Norton, *J. Catalysis*, 1964, **3**, 252

The Vapour Phase Deposition of Rhodium

Interest in the vapour phase deposition of the platinum metals has been hindered by the difficulty of establishing the most suitable volatile compounds of these metals on which to base a reliable process. For applications where electrodeposition or other methods of coating cannot be employed, or can be used only with considerable difficulty, a vapour phase technique would present considerable potentialities, and a paper by Hemert, Spendlove and Sievers (*J. Electrochem. Soc.*, 1965, **112**, (11), 1123) is of value in this connection.

These workers found that certain fluorcarbon-β-diketonate metal chelates are not only highly volatile but are thermally stable and are readily reduced to metal at atmo-

spheric pressure at temperatures as low as 250°C.

Thin films of copper, nickel and rhodium were produced in a simple apparatus in which two different temperatures could be maintained simultaneously in different sections. The gaseous chelate was transported by a stream of hydrogen to the reduction zone, where it was reduced to metal.

The deposits obtained adhered very well to the glass tubes on which they were formed, even though the tubes had not been specially cleaned or etched. They were all mirror-like on both surfaces, and all were electrically conductive. They were ductile and when scraped from the substrate could be folded without fracture.