

Ruthenium-Platinum Oxide Catalysts

HIGH ACTIVITY IN HYDROGENATION REACTIONS

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Hydrated platinum oxide ($\text{PtO}_2 \cdot \text{H}_2\text{O}$) prepared by the method originally devised by Adams (1) has been used as a catalyst for organic hydrogenations for some four decades. When suspended in a liquid, it is rapidly reduced to a finely divided metal by hydrogen at room temperature and atmospheric pressure, and may be introduced into the reaction system without pre-reduction. The Adams technique, which is essentially the oxidation of a suitable salt in molten sodium nitrate at 400 to 550°C, is applicable also to rhodium and palladium, and the recent publications by Nishimura and his colleagues of results on mixed rhodium-platinum oxides (2) have shown them to have properties not possessed by either oxide separately. This work has encouraged us to examine a number of binary mixed oxides prepared by the Adams method, and this report summarises our findings on the ruthenium-platinum system.

Mixed ruthenium-platinum oxides were prepared by adding small portions of an intimate mixture of ammonium chloroplatinate and ruthenium trichloride to molten sodium nitrate at 400°C. Slight loss of ruthenium as the volatile tetroxide occurred. Subsequent steps in the preparation were precisely the same as those employed in the preparation of platinum oxide.

It was found that compositions in which the nominal Ru:Pt ratio lay

between 1:40 and 1:1 on an atomic basis had after reduction catalytic activity in a number of reactions much superior to that of pure platinum oxide. Figures 1 and 2 show how the rates of reduction of nitrobenzene, *o*-nitroaniline, methyl butynol (2-methyl but-3-yne-2-ol), maleic acid and cyclo-

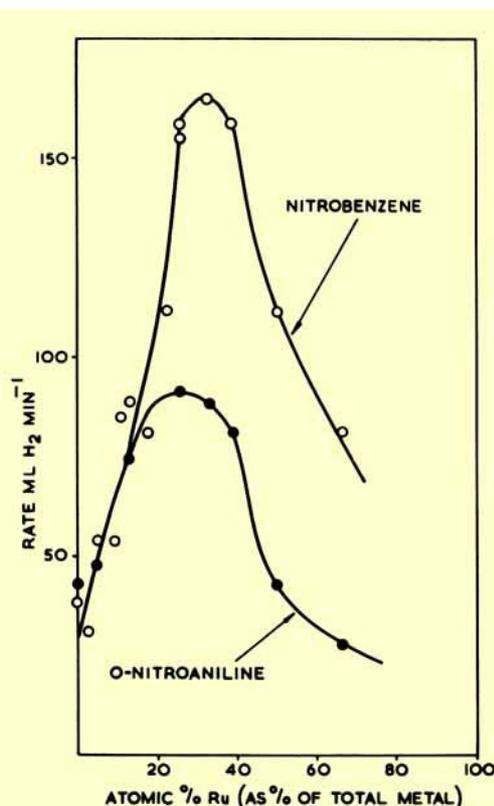


Fig. 1 Activity of reduced ruthenium-platinum oxides in the reduction of nitrobenzene and *o*-nitroaniline

hexanone vary with the nominal ruthenium content of the mixed oxide, using a fixed weight of the catalyst.

Fig. 1 shows that the rate of reduction of nitrobenzene attains a maximum when the atomic Ru:Pt ratio is about 1:2, this maximum rate being about five times greater than the rate given by pure platinum oxide. With *o*-nitroaniline the maximum occurs when the atomic Ru:Pt ratio is about 1:3, although here the enhancement factor is only about two.

The composition at which maximum rates occur varies quite widely from one substrate to another, as is seen in Fig. 2. For methyl butynol the maximum occurs when the atomic Ru:Pt ratio is 1:20, for maleic acid at 1:4; and for cyclohexanone at about 1:1. The enhancement factors lie between 2 and 3.

Maxima were also observed in the hydrogenation of the following substances, at the atomic Ru:Pt ratios quoted in brackets: cyclohexene (2:3), acetophenone (1:2), and pyridine (1:20). No significant variation of rate with composition was observed with benzene.

The nature of the reduced catalyst has not yet been fully explored, but there is some evidence which suggests that the two metals are alloyed rather than being simply in admixture. Ruthenium dioxide is known not to be reduced under the conditions of these experiments, and hence if the activity were solely due to the platinum component the activity would be expected to fall with increasing ruthenium content. This is not what is observed. It is likely that those compositions containing a high proportion of ruthenium would have shown a higher activity in some of our test reactions had they been more vigorously reduced. Surface area measurements on both the mixed oxides and the products of their reduction are now under way, but it is quite evident that variation in surface area cannot alone account for the

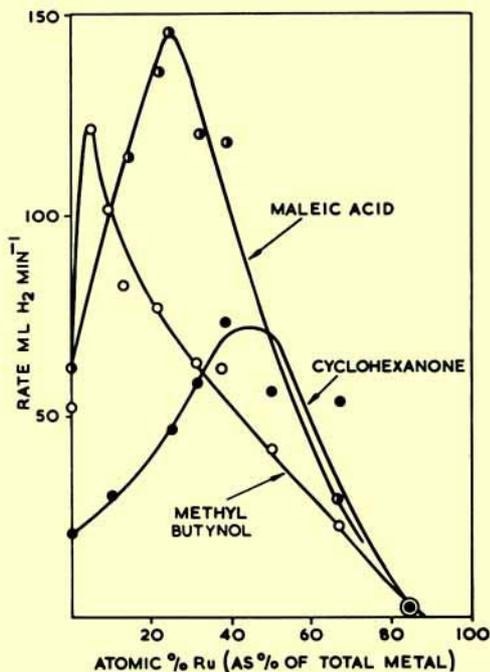


Fig. 2 Activity of reduced ruthenium-platinum oxides in the hydrogenation of methyl butynol, maleic acid and cyclohexanone

observed results, which show widely differing activity-composition curves as will be seen from Fig. 2.

Other methods of preparation of active ruthenium-platinum catalysts are also being investigated, for example, reduction in the liquid phase of the oxides or an aqueous solution of the metal chlorides with sodium borohydride. Raney ruthenium-platinum has also been prepared.

There seems little doubt that effects due to the electronic interaction of substrate molecules with the catalyst surface are being exhibited, and we hope that the more detailed study of this system which is now in progress will illuminate the relevance of the electronic constitution of metals and alloys to their catalytic properties.

References

- 1 *Platinum Metals Rev.*, 1962, 6, 150
- 2 See for example S. Nishimura, *Bull. Chem. Soc. Japan*, 1961, 34, 1544