Ruthenium-Platinum Oxide Catalysts for Hydrogenation Reactions

A CRITICAL COMPARISON OF PUBLISHED RESULTS

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Since the publication of earlier papers from the Johnson Matthey Research Laboratories on the catalytic properties of mixed platinum group metal catalysts, two other groups have published their findings. These are in certain respects in disagreement with each other and with the original work and results relating to the ruthenium-platinum system are critically discussed in this paper.

A technique for the preparation of intimate homogeneous binary mixtures of oxides of the platinum group metals by a modification of the Adams method has been described in a previous publication (1). These mixed oxides are in the main easily reduced by hydrogen under ambient conditions to yield what we believe to be finely divided alloys of the two metals, and many of the catalysts produced in this way are much more active in a variety of hydrogenations than either component oxide alone. Our previous publications describe results obtained with ruthenium-platinum catalysts (1) and a number of other mixed metals (2).

Two other groups of workers have since reported their own work on these systems. The results published (3) by D. V. Sokol'skii and his associates at Alma Ata for the ruthenium-platinum system are in broad agreement with ours in the composition range which we originally covered, but they reported a further substantial activity maximum (at about 90 per cent ruthenium) which we had not observed. The work of P. N. Rylander and his colleagues (4) of Engelhard Industries on this system is in complete and utter disagreement with both ours and Sokol'skii's, but because the conditions have not been identical (and in particular the other groups have used other solvents) we decided to check their observations. The purpose of this paper is to give a brief summary of our further work on the ruthenium-platinum system and to compare it critically with the other published results.

Surface Areas

It is unlikely that the reported differences in catalytic properties are significantly due to differences in the surface areas of the starting oxides. Values of surface areas given by the Engelhard workers (4) (their method is not described) are in approximate agreement with ours obtained using low temperature nitrogen adsorption with a Perkin-Elmer-Shell Sorptometer (e.g. about 100 m^2g^{-1} for PtO_2): Sokol'skii's values (3), obtained by low temperature adsorption of air, are lower by a factor of about 2.5, but all groups agree there is a tendency for the area of the oxide to fall with increasing ruthenium content. In our hands the surface area for a given composition is not closely reproducible from one preparation to another, the variation being much greater than is the case with catalytic activity. We therefore consider it inappropriate to quote specific activities using areas of the oxides.

Incidentally neither Rylander nor Sokol'skii appear to have assayed their mixed oxides.

Nominal and Actual Ruthenium Contents (wt%) of Mixed Ruthenium-Platinum Oxides	
Nominal	Actual
2.5	1.63
5	2.75
10	6.32
20	15.2—16.9
50	43.8

We find a substantial loss of ruthenium during the preparation, presumably as the volatile tetroxide. The figures given in the table are representative of our findings.

Reduction of Aromatic Nitro-compounds

In our earlier publications (1, 2), we demonstrated the existence of a very sharp activity maximum for the reduction of nitro-benzene in methanol at 25 atomic per cent ruthenium: a similar but less pronounced maximum was shown with o-nitroaniline. We have confirmed the generality of the maximum in this position by obtaining results for 2,4-dinitrotoluene in acetone/isopropanol (see Figure 1): the rate at the maximum is about three times less than for nitrobenzene. Sokol'skii and his associates (3) report results for the reduction of o-nitrophenol in 96 per cent ethanol. These are also shown in Figure 1, as are our own rates for the reduction of this compound in methanolic solution. It is clear that the reaction is enormously faster in methanol than in 96 per cent ethanol (by a factor of about 30): it is however known that water can be a powerful catalyst poison in the reduction of aromatic nitro-compounds. However, Sokol'skii observes a maximum at about 35 atomic per cent ruthenium, and, significantly, a second smaller maximum at about 80 atomic per cent ruthenium. As our catalysts are inactive when containing more than 85 atomic per cent ruthenium because they are not reduced under our experimental conditions, we infer that Sokol'skii's catalysts are pre-reduced in some manner, although his publications give no details.

Now the Russian authors also report that the second maximum in the reduction of o-nitrophenol is much more pronounced when the solvent is aqueous decinormal KOH, i.e., when the reactant is the o-nitrophenoxide ion. In order to check this and to obtain further information on the effect of pre-reduction of the catalyst, we have studied the reduction of o-nitrophenol in this solvent in the normal manner and also using catalyst pre-reduced by shaking in hydrogen under ambient conditions before adding the reactant. The results, together with Sokol'skii's, are shown in Figure 2. With catalysts not pre-
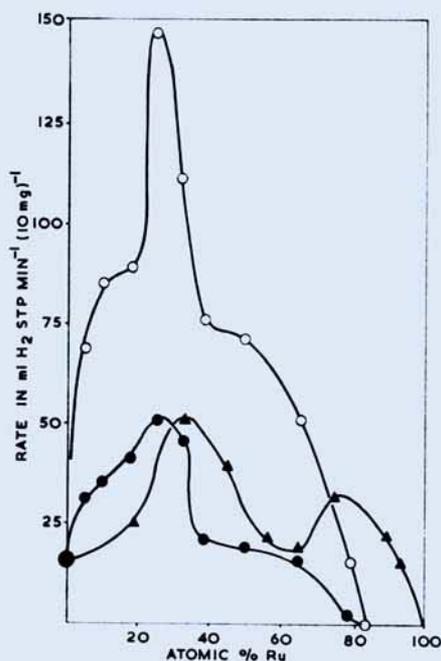

Fig. 1 Hydrogenation of aromatic nitro-compounds in the presence of ruthenium-platinum catalysts.

○ o-Nitrophenol in methanol

▲ o-Nitrophenol in 96% ethanol – results of Sokol'skii and associates multiplied by 10

● 2,4-Dinitrotoluene in acetone/isopropanol

Note: rates are plotted against nominal rather than actual atomic composition to facilitate comparison of our work with that of others; this applies also to Figs 2 and 3.

reduced we find a broad maximum between 10 and 50 atomic per cent ruthenium with a slight dip which may or may not be genuine. Pre-reduction lowers the activity slightly in this region but certainly causes ruthenium-rich catalysts to be active, although our second maximum is far less marked than is Sokol'skii's. As the solvents are identical in this case, differences can only be caused by differences in catalyst preparation or experimental procedure.

We turn now to examine the results of the Engelhard workers. Their results for the reduction of nitrobenzene in glacial acetic acid are so much at variance with ours obtained using methanol as solvent, that we
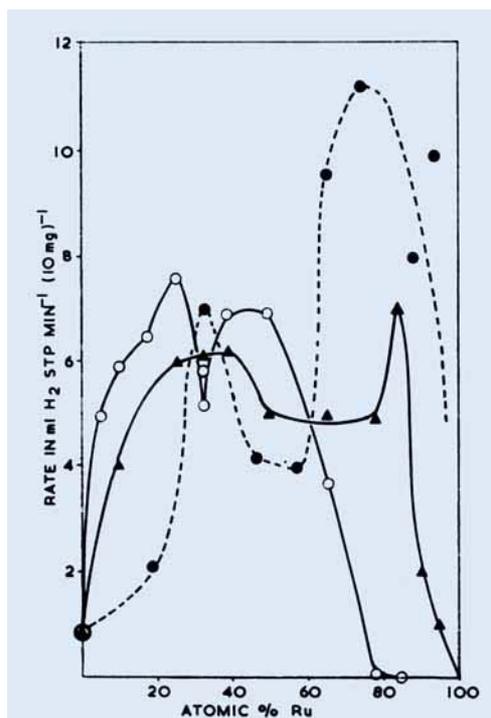
Fig. 3 Hydrogenation of nitrobenzene in the presence of ruthenium-platinum catalysts.
  A. In methanol
  B. In glacial acetic acid
  C. In glacial acetic acid according to Rylander and associates

Fig. 2 Hydrogenation of o-nitrophenol in the presence of ruthenium-platinum catalysts.
  ○ In 0.1N KOH using catalysts not pre-reduced
  ▲ In 0.1N KOH using pre-reduced catalysts
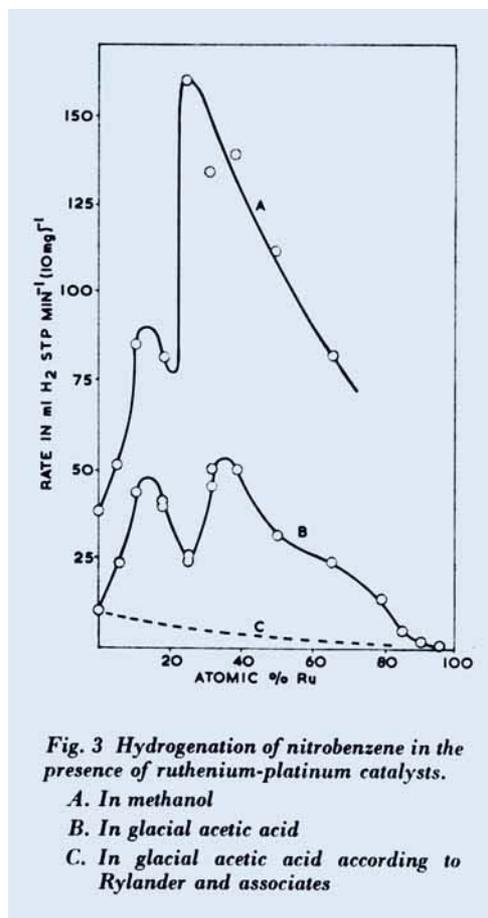 ● Results of Sokol'skii and associates in 0.1N KOH

decided to repeat our work using their solvent. These results are shown in Figure 3. Unfortunately it is not possible to make a direct comparison of rates even for PtO_2 as the Engelhard papers (4), do not mention the weight of catalyst used: however it would appear from our results that theirs refer to 10 mg of catalyst and the line through their points is shown in Figure 3 based on this assumption. The disagreement, which is profound and inexplicable, is not commented on by Rylander. Glacial acetic acid is anyhow an unsatisfactory solvent, the maximum rate of nitrobenzene hydrogenation in it being some three times less than when methanol is the solvent (see also Figure 3).

It is abundantly clear that rates of hydrogenation with this catalyst are very much

dependent on the kind of solvent used, but other factors must be operating: their nature will only be revealed by further work.

Other Reactions

Sokol'skii and his associates report (3) for the hydrogenation of olefins (cyclohexene and 1-heptene) using ruthenium-platinum catalysts that maximum rates occur at 45 and 88 atomic per cent ruthenium. We originally showed the existence of a maximum rate for the hydrogenation of maleic acid in methanol at about 30 atomic per cent ruthenium and have since found a maximum at about the same concentration in glacial acetic acid.

One of the interesting features of our earlier work was that, with acetylenic substances such as methylbutynol, maximum rates occurred with very low concentrations of ruthenium: the Engelhard group report (4) a similar observation (almost the only point of agreement between us) but their maximum rate is only about 20 per cent greater than for PtO_2 whereas we found a maximum rate about 2.2 times greater.

Other Cata ᵧ ᵧ ᵤs

Comparison of our results with those of the Engelhard group for rhodium-platinum catalysts again demonstrates the existence of a large solvent effect. With this system glacial acetic acid is a much better solvent than methanol for nitrobenzene hydrogenation: with methanol we find rates which vary somewhat erratically with catalyst composition, the maximum rate (at 39 atomic per cent rhodium) being only about 50 per cent greater than for PtO_2. However, with glacial acetic acid as solvent the maximum rate occurs at the same composition but is four times greater than for PtO_2. Rylander reports the factor to be about 2.5. Again we cannot compare absolute rates for the reasons given.

Conclusions

Substantial and inexplicable differences are shown between the results of the various groups which have worked on mixed platinum group metal catalysts. Solvent effects are partly responsible, but the precise method of preparing the mixed oxides and differences in experimental procedure are other possible factors which may account for the discrepancies.

Ruthenium-platinum oxide catalysts, their preparation and use, are covered by British Patent Nos 1,099,406 and 1,016,058 and U.S. Patent No. 3,305,402, and are the subject of pending patent applications in a number of other countries.

References

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Complexes of Substituted Olefins with Salts of the Platinum Metals

One of the small but intriguing parts of organometallic chemistry concerns the complexes formed between salts of the transition metals—more particularly those of the platinum metals—and substituted olefins. The discovery of this class of compound has not only advanced our knowledge of chemistry and of chemical bonding, but has stimulated our understanding of catalytic processes both in solution and at solid surfaces. A recent review by Richard Jones of the ICI Petrochemical and Polymer Laboratory (*Chem. Rev.*, 1968, **68**, 785) provides a thorough survey of this field. Among the type of substituents discussed are halogens, where perfluoro-olefins behave in some respects quite differently from simple olefins, and amine and cyanide groups, both of which may also chelate to the central metal atom. Complexes of this type provide an increased range of stabilities by comparison with their unsubstituted analogues, and may well find industrial uses in the tailor-making of catalysts of specific activity.