Rhodium-Platinum Oxide as a Catalyst for the Hydrogenation of Organic Compounds. II[1]. *Catalyst Preparation and Effects of Platinum in Rhodium-Platinum Oxide*

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It was reported previously[1-3] that rhodium-platinum(3 : 1) oxide prepared exactly in the same way as Adams platinum oxide is easily reduced with hydrogen to the metals at the ordinary temperature and pressure and that the resulting rhodium-platinum black is an excellent catalyst retaining the nature of a pure rhodium catalyst and is substantially superior to Adams platinum and palladium catalysts both in activity and in selectivity in the hydrogenation of various organic compounds.

It has been found that the activity of rhodium-platinum(3 : 1) oxide and also that of rhodium oxide are considerably enhanced by fusing the corresponding chlorides with sodium nitrate for a shorter time at a lower temperature than as directed in the preparation of platinum oxide[4]. The rhodium-platinum(3 : 1) catalyst prepared in this way is not only more active, but also more easily dissolved in aqua regia than reported previously. This fact prompted the author to prepare a catalyst which retains the nature of a rhodium catalyst and can be completely recovered with aqua regia. Rhodium-platinum oxide of various compositions has been prepared by the improved procedure and the activity and selectivity have been studied in the hydrogenation of toluene and acetophenone in acetic acid. The results are summarized in Table I. The catalysts containing 70 to 90% of rhodium are the most active and selective. On the other hand, those containing about 30% or more of platinum dissolve on gently heating in aqua regia without leaving any insoluble residue. Thus the requirements mentioned above are satisfied to a large extent by the catalyst consisting of 70% of rhodium and 30% of platinum, which dissolves in aqua regia practically with no residue, and yet is nearly as active and as selective as rhodium-platinum(3 : 1) oxide.

Though rhodium oxide is not easily reduced with hydrogen as noted previously[2], that prepared by the improved procedure can be reduced to the metal in 3~4 hr. at 30°C or in about 1 hr. at 45~50°C in acetic acid under the atmospheric pressure of hydrogen. The resulting rhodium black, however, is unexpectedly less active than rhodium-platinum (3 : 1) oxide as shown in the hydrogenation of toluene. The proportion of hydrogenolysis in the hydrogenation of acetophenone is somewhat greater with rhodium oxide than with rhodium-platinum(3 : 1) oxide (see Table I). Thus, the platinum in rhodium-platinum oxide promotes the reduction of the oxide to the metals, makes the resulting catalyst more active and selective than the pure rhodium catalyst, and makes it possible to recover the metals with aqua regia.

1) Part I: S. Nishimura, This Bulletin, **34**, 32 (1961).
2) S. Nishimura, ibid., **33**, 566 (1960).
3) S. Nishimura, T. Onoda and A. Nakamura, ibid., **33**, 1356 (1960).
4) R. Adams, V. Voorhees and R. L. Shriner, "Organic Syntheses", Col. Vol. I, 2nd Ed., John Wiley & Sons, Inc., New York (1941), p. 463.

TABLE I. CATALYTIC HYDROGENATION OF TOLUENE AND OF ACETOPHENONE WITH RHODIUM-PLATINUM OXIDE OF VARIOUS COMPOSITIONS[a]

Catalyst		Time for the reduction of oxide to metal	Hydrogenation of toluene (0.921 g.)		Hydrogenation of acetophenone (0.601 g.)	
Rh(%)	Pt(%)	min.	Initial rate[b] ml./min.	Time min.	H_2 uptake mol./mol.	Time min.
100	0	210	88	23	4.08	30
90	10	50	110	15	4.03	20
80	20	30	106	16	4.02	22
75	25	24	108	15	4.02	20
70	30	20	103	16	4.02	20
60	40	16	91	16	4.05	24
50	50	11	87	17	4.08	36
25	75	5	49	25	4.15	50
0	100	2	19	83	4.65	75

a) Each hydrogenation was carried out with 50 mg. of oxide in 20 ml. of acetic acid at 30°C under the atmospheric pressure of hydrogen. The substance to be hydrogenated was added after the oxides was reduced to the metal.

b) Initial rate refers to 50 mg. of catalyst metal.

Procedure for the Preparation of Rhodium-Platinum (7 : 3) Oxide. — A mixture of the chlorides corresponding to 0.30 g. of rhodium and 0.13 g. of platinum in the weights of the metals is fused with 20 g. of sodium nitrate in the same way as in the preparation of platinum oxide[5]. After a violent evolution of the oxides of nitrogen has almost subsided, the temperature is raised and kept at 460~480°C for about 10 min. After cooling, the solidified mass is rinsed in distilled water. The solid is collected, washed with 100 ml. of 0.5% aqueous sodium nitrate, and then dried over calcium chloride. The yield is 0.665 g., which is quantitative on the basis of the metal content (65%) of the oxide.

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5) Cf. Ref. 4, p. 463.