The Hydroxide-Blacks of Ruthenium and Rhodium as Catalysts for the Hydrogenation of Organic Compounds. I. Their Catalytic Activity and Selectivity in the Hydrogenation of Some Aromatic Compounds[*1]

By Yuzuru TAKAGI, Takatoshi NAITO and Shigeo NISHIMURA[*2]

(Received May 7, 1965)

Recently it has been shown in many studies that ruthenium and rhodium catalysts or those containing these metals are outstanding in catalytic activity and selectivity in the hydrogenation of various organic compounds. High activities and/or high selectivities have been reported, for instance, in the hydrogenation of aromatic and heterocyclic compounds,1) olefins,2) carbonyl compounds,1c,1e,3) nitriles,4) and carboxylic acids to alcohols,5) in the selective production of alicyclic primary amines,6) in the selective hydrogenation of the compounds susceptible to hydrogenolysis,1e,4,7) and in the selective cis-hydrogenation of substituted aromatic compounds.8) There are also many other examples in which these catalysts have been shown to be useful.

The hydrogenations mentioned above are mostly concerned with the use of either the catalysts from the oxides of ruthenium and rhodium, those prepared by the reduction of the chlorides of ruthenium and rhodium with sodium borohydride, or the ruthenium and rhodium catalysts supported on various carriers. It appears that no study has yet been concerned with the use of the hydroxide-black catalysts of ruthenium and rhodium. The hydroxide of ruthenium or rhodium is easily prepared as, respectively, a black or a yellow precipitate, by adding a slight excess of a sodium hydroxide solution to a hot aqueous solution of ruthenium or rhodium chloride. The hydroxides of ruthenium and rhodium thus prepared have been found to exhibit excellent catalytic activity in the hydrogenation of various organic compounds when they are reduced to the metals in the presence of the compounds to be hydrogenated.

In this paper the activity and/or the selectivity of these hydroxide-black catalysts have been studied in the hydrogenation of toluene, benzoic acid, *o*-xylene, hydroquinone dimethyl ether and phenyl ether. The results are summarized in Tables I to V, along with those obtained with the oxides of ruthenium and rhodium. The mixed ruthenium-rhodium hydroxides were also prepared from mixtures of ruthenium chloride and rhodium chloride by the same method; the results with these catalysts are also included in the tables.

The hydroxide-catalyzed hydrogenations of the aromatic compounds proceed rapidly at 85 to 100°C under a high hydrogen pressure. Usually only a very small amount of the hydroxide is required for hydrogenation to be completed within a short time. Though a small amount of acetic acid was added in each hydrogenation in order to neutralize the trace of alkaline substances remaining in the catalysts, the hydroxide-catalyzed hydrogenations generally proceed smoothly without the addition of acetic acid (see the example shown in Table I). This fact, together with other observations,[*3] suggests that the hydroxides of ruthenium and rhodium

---

[*1] Presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

[*2] Present address: Department of Industrial Chemistry, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo.

1) a) E. F. Rosenblatt, U. S. Pat. 2675390 (1954). b) L. D. Freedman, G. O. Doak and E. L. Petit, *J. Am. Chem. Soc.*, **77**, 4262 (1955). c) G. Gilman and G. Cohn, "Advances in Catalysis," Vol. 9, Academic Press Inc., New York (1957), p. 733. d) A. Amano and G. Parravano, ibid., Vol. 9 (1957), p. 716. e) S. Nishimura, This Bulletin, **33**, 566 (1960); **34**, 32 (1961). f) M. Freifelder and G. R. Stone, *J. Org. Chem.*, **26**, 3805 (1961); M. Freifelder, R. M. Robinson and G. R. Stone, ibid., **27**, 284 (1962).

2) O. Beeck, *Discussions Faraday Soc.*, **8**, 118 (1950); G. C. A. Schuit and L. L. van Reijen, "Advances in Catalysis," Vol. 10, Academic Press Inc., New York (1958), p. 242; H. C. Brown and C. A. Brasn, *J. Am. Chem. Soc.*, **84**, 1494 (1962).

3) G. G. Boyers, U. S. Pat. 2868847 (1959) (*Chem. Abstr.*, **53**, 9084d (1959)); A. A. Balandin, N. A. Vasyunina, G. A. Barysheva and S. V. Chepigo, *Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk*, **1957**, 392 (*Chem. Abstr.*, **51**, 14260f (1957)); E. Breitner, E. Roginski and P. N. Rylander, *J. Org. Chem.*, **24**, 1855 (1959).

4) M. Freifelder, *J. Am. Chem. Soc.*, **82**, 2386 (1960).

5) J. E. Carnahan, T. A. Ford, W. F. Gresham, W. E. Grigsby and G. F. Hager, ibid., **77**, 3766 (1955).

6) L. C. Behr, J. E. Kirby, R. N. MacDonald and C. W. Todd, ibid., **68**, 1296 (1946); G. M. Whitman, U. S. Pat. 2606925 (1952) (*Chem. Abstr.*, **47**, 3874i (1953)); A. E. Barkdoll, D. C. England, H. W. Gray, W. Kirk, Jr. and G. M. Whitman, *J. Am. Chem. Soc.*, **75**, 1156 (1953); M. Freifelder and G. R. Stone, *J. Org. Chem.*, **27**, 3568 (1962); Abbott Laboratories, Brit. Pat. 881512 (1961) (*Chem. Abstr.*, **56**, 11465f (1962)); S. Nishimura and H. Taguchi, This Bulletin, **36**, 873 (1963).

7) a) H. A. Smith and R. G. Thompson, "Advances in Catalysis," Vol. 9, Academic Press Inc., New York (1957), p. 727; S. Nishimura et al., This Bulletin, **33**, 1356 (1960); **36**, 318, 353 (1963); J. H. Stocker, *J. Org. Chem.*, **27**, 2288 (1962); H. W. Arnold, U. S. Pat. 2555912 (1951) (*Chem. Abstr.*, **46**, 3074f (1952)); G. E. Ham and W. P. Coker, *J. Org. Chem.*, **29**, 194 (1964). b) Y. Takagi, T. Naito and S. Nishimura, This Bulletin, **37**, 585 (1964).

8) A. W. Burgstahler and Z. J. Bithos, *J. Am. Chem. Soc.*, **82**, 5466 (1960); "Organic Syntheses," Vol. 42, 62 (1962); S. Nishimura and H. Taguchi, This Bulletin, **36**, 353 (1963); F. Hartog and P. Zwietering, *J. Catalysis*, **2**, 79 (1963).

[*3] A marked difference in selectivity in the hydrogenation of nitriles and aniline was observed between the hydroxides and the oxides; this difference may be attributed to the difference in the alkali contents of the catalysts (to be described in following papers).

TABLE I. HYDROGENATION OF TOLUENE[a]

Catalyst	Amount mg.	Additive, ml.	Time for hydrogenation[b] min.
Ru hydroxide	25	AcOH, 0.05	28
Ru hydroxide	10	H_2O, 1	9
Ru hydroxide	10	H_2O, 3	6
Ru hydroxide	10	H_2O, 6	4
Ru hydroxide	5	H_2O, 1 + AcOH, 0.05	12
Ru hydroxide	1	H_2O, 1 + AcOH, 0.05	17
Rh hydroxide	5	H_2O, 1 + AcOH, 0.05	11
Ru dioxide	5	H_2O, 1 + AcOH, 0.05	18
Rh oxide	5	H_2O, 1 + AcOH, 0.05	11

a) Toluene (9.2 g.) was hydrogenated at 85°C and 80 to 100 kg./cm² of hydrogen pressure.

b) The product consisted exclusively of methylcyclohexane throughout the runs, containing neither toluene nor any other compound.

TABLE II. HYDROGENATION OF BENZOIC ACID[a]

Catalyst	Amount mg.	Solvent ml.	Time for hydrogenation[b] min.
(1:1) Ru-Rh hydroxide	4	H_2O, 15	180
Rh hydroxide	4	H_2O, 15	130
Rh oxide	4	H_2O, 15	120

a) Benzoic acid (12 g.) was hydrogenated at 100°C and 70 to 100 kg./cm² of hydrogen pressure.

b) The product (cyclohexanecarboxylic acid) was not isolated, but the hydrogen uptake was quantitative in each run.

contain much less alkali than do the oxides of ruthenium and rhodium, even though the hydroxides were precipitated from an alkaline solution.

The promoting action of water reported in the hydrogenation with a supported ruthenium catalyst[9] was also observed in the ruthenium hydroxide-catalyzed hydrogenations (see Tables I and IV). In the presence of water the ruthenium hydroxide was nearly as active as or even more active than the rhodium hydroxide in the hydrogenation of toluene and *o*-xylene, whereas the addition of water slightly retarded the hydrogenation of hydroquinone dimethyl ether with rhodium hydroxide. Generally the catalytic activity of ruthenium hydroxide is considerably greater than that of ruthenium dioxide,[*4] and rhodium hydroxide is nearly as active as the rhodium oxide of the Adams type.[11] No appreciable co-activation effect of ruthenium and rhodium was observed in hydrogenation with the mixed ruthenium-rhodium hydroxides, although such an effect was reported with a supported ruthenium-rhodium catalyst.[12]

As may be seen from Tables III and IV, ruthenium hydroxide is more selective than the rhodium catalysts in the cis-hydrogenation of *o*-xylene[*5] and hydroquinone dimethyl ether. It should be noted that the presence of water increases the yield of *cis*-1, 4-dimethoxycyclohexane in the hydrogenation of hydroquinone dimethyl ether. Both ruthenium and rhodium hydroxides give good yields of the corresponding saturated ethers in the hydrogenation of hydroquinone dimethyl ether and phenyl ether, which are both very easily susceptible to the hydrogenolysis of the C–O linkage (Table

TABLE III. HYDROGENATION OF *o*-XYLENE

Catalyst	Amount, mg.	Additives, ml.	Time for hydrogenation min.	cis/trans ratio of 1,2-dimethylcyclohexane[b]
Ru hydroxide	5	H_2O, 1 + AcOH, 0.05	16	12.3
(3:1) Ru-Rh hydroxide	5	H_2O, 1 + AcOH, 0.05	16	10.3
(1:1) Ru-Rh hydroxide	5	H_2O, 1 + AcOH, 0.05	16	10.2
(1:3) Ru-Rh hydroxide	5	H_2O, 1 + AcOH, 0.05	18	9.3
Rh hydroxide	5	H_2O, 1 + AcOH, 0.05	23	9.5
Ru dioxide	5	H_2O, 1 + AcOH, 0.05	26	11.2

a) *o*-Xylene (10.6 g.) was hydrogenated at 85°C and 80 to 100 kg./cm² of hydrogen pressure.

b) The yield of 1,2-dimethylcyclohexane was quantitative in each run.

---

[9] P. N. Rylander, N. Rakoncza, D. Steele and M. Bollinger, *Engelhard Ind. Tech. Bull.*, **4**, 95 (1963).

[*4] The ruthenium dioxide used in this study was prepared by the method of Pichler and Buffleb.[10] The oxide of ruthenium may also be prepared by the Adams method (cf. G. C. Bond and D. E. Webster, *Proc. Chem. Soc.*, **1964**, 398), but the resulting catalyst was far less active than the oxide of Pichler and Buffleb in the hydrogenation of toluene. The oxide obtained by the Adams method shows peaks at $2\theta=28°$ and 35° in the X-ray diffraction analysis using Cu-K_α radiation; these peaks are consistent with those of ruthenium dioxide reported in the literature. Pichler's dioxide and ruthenium hydroxide do not show any distinct diffraction patterns corresponding to the oxide of ruthenium. The oxide obtained by the Adams method does not dissolve in hot concentrated hydrochloric acid, whereas Pichler's dioxide partly, and ruthenium hydroxide rather easily, dissolve in the acid. These facts suggest that Pichler's dioxide is probably a mixture of the oxide and the hydroxide of ruthenium.

[10] H. Pichler and H. Buffleb, *Brennstoff-Chem.*, **21**, 257 (1940).

[11] S. Nishimura, This Bulletin, **34**, 1544 (1961).

[12] P. N. Rylander and D. R. Steele, *Engelhard Ind. Tech. Bull.*, **3**, 91 (1962).

[*5] Since rhodium oxide gives a better yield of *cis*-1, 2-dimethylcyclohexane than platinum oxide under similar conditions (unpublished; cf. Ref. 8), the order of selectivity in the cis-hydrogenation of *o*-xylene will be as follows: ruthenium>rhodium>platinum.

TABLE IV. HYDROGENATION OF HYDROQUINONE DIMETHYL ETHER[a]

Catalyst	Amount, mg.	Additives, ml.	Time for hydrogenation min.	1,4-Dimethoxycyclohexane	
				% yield[b]	cis/trans ratio
Ru hydroxide	20	AcOH, 0.05	80% hydrogenation/80 min.	—	3.0
Ru hydroxide	20	H_2O, 5 + AcOH, 0.05	19	78	4.0
(3:1) Ru-Rh hydroxide	20	AcOH, 0.05	23	86	3.3
(3:1) Ru-Rh hydroxide	20	H_2O, 5 + AcOH, 0.05	13	78	3.6
(1:1) Ru-Rh hydroxide	20	AcOH, 0.05	19	91	3.0
(1:1) Ru-Rh hydroxide	20	H_2O, 5 + AcOH, 0.05	11	78	3.6
(1:3) Ru-Rh hydroxide	20	AcOH, 0.05	16	89	3.1
(1:3) Ru-Rh hydroxide	20	H_2O, 5 + AcOH, 0.05	12	78	3.3
Rh hydroxide	20	AcOH, 0.05	8	98	2.8
Rh hydroxide	20	H_2O, 5 + AcOH, 0.05	12	76	3.2
Rh oxide	20	AcOH, 0.05	8	97	2.8
Ru dioxide	20	AcOH, 0.05	10% hydrogenation/60 min.	—	—

a) Hydroquinone dimethyl ether (14 g.) was hydrogenated at 85°C and 80 to 100 kg./cm² of hydrogen pressure.

b) Smaller yields in the presence of water result from partly hydrolysis during the hydrogenation.

TABLE V. HYDROGENATION OF PHENYL ETHER[a]

Catalyst	Amount, mg.	Additive, ml.[b]	Time for hydrogenation min.	% yield of cyclohexyl ether
Ru hydroxide	50	AcOH, 0.05	120	77.5
(3:1) Ru-Rh hydroxide	50	AcOH, 0.05	95	79.0
(1:1) Ru-Rh hydroxide	50	AcOH, 0.05	25	84.0
(1:3) Ru-Rh hydroxide	50	AcOH, 0.05	27	83.0
Rh hydroxide	50	AcOH, 0.05	12	86.5
Ru dioxide	50	AcOH, 0.05	42% hydrogenation/200 min.	—
Rh oxide	50	AcOH, 0.05	8	84.5

a) Phenyl ether (10 g.) was hydrogenated at 85°C and 80 to 100 kg./cm² of hydrogen pressure.

b) Addition of water caused the hydrolysis of phenyl ether to a large extent.

IV and V). The rhodium hydroxide is somewhat more selective than the ruthenium hydroxide in these hydrogenations, the results with it being consistent with those reported previously for the oxides of ruthenium and rhodium.[7b] As can be seen from Tables III to V, the selectivities of the mixed ruthenium-rhodium hydroxides are generally those which would be expected from their compositions and not greater than that of either ruthenium hydroxide or rhodium hydroxide.

The results described above show that the hydroxide-black catalysts of ruthenium and rhodium are excellent catalysts in their activity and selectivity in the hydrogenation of the aromatic compounds. The method of preparing the hydroxides is very simple, and the resulting catalysts are nearly as active as or even more active than the corresponding oxide catalysts. Moreover, the catalysts containing much less alkali than the oxides may easily be obtained. Further studies will be reported in following papers.

Experimental

Catalysts.—The hydroxides of ruthenium, rhodium, and ruthenium-rhodium were prepared by vigorously stirring a slight excess of a 10% sodium hydroxide solution into an about 1% aqueous solution of the metal chloride at 85 to 90°C. The precipitate thus formed was collected on a filter paper, washed with distilled water many times until the pH of the filtrate finally became 7.8, and then dried in a vacuum at room temperature. The yields were quantitative as judged on the basis of the metal contents of the hydroxides (see below). Ruthenium dioxide was prepared according to the method of Pichler and Buffleb[10] by the fusion of ruthenium metal powder with potassium hydroxide and potassium nitrate, followed by reduction with methyl alcohol. Rhodium oxide was prepared by a modified Adams method[11] by the fusion of rhodium chloride with sodium nitrate at 460 to 480°C. The metal contents of the hydroxides and the oxides were estimated from the decrease in their weights when they were reduced to the metals in an atmosphere of hydrogen, using a thermobalance. The metal contents of ruthenium hydroxide, ruthenium dioxide, rhodium hydroxide, and rhodium oxide were 65, 75, 57, and 69% respectively.

Hydrogenation. — A 100 ml. bomb of an electromagnetically-stirring-type was used in all the hydrogenations. The bomb was charged with a 100 kg./cm^2 pressure of hydrogen and immersed in water maintained at 85°C during the hydrogenation, except in the case of benzoic acid. The hydrogenation of benzoic acid was carried out at 100°C with the use of water as the solvent, because at temperatures below 100°C the rate was too slow, probably because of the low solubility of benzoic acid in water. All the products, except cyclohexanecarboxylic acid, were analyzed by means of gas chromatography using a column containing PEG-6000.

The authors wish to express their gratitude to Professor Kozo Hirota of this Institute for his continued encouragement. The authors are also indebted to the Mitsubishi Chemical Industries Co., Ltd., for its financial support.

The Institute of Physical and Chemical Research
Bunkyo-ku, Tokyo