Reduction of Organic Compounds with Urushibara Catalysts under High Pressure. VII[1]*. Feature of Various Urushibara Catalysts as Revealed in the Reduction of Benzophenone*

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In the previous paper[2] of this series, catalytic reductions of ketones under high pressure with Urushibara nickel **B** were reported. In the present paper, reduction of benzophenone with various Urushibara catalysts under various conditions was investigated.

The preparation of the Urushibara nickel catalyst has been successively modified, and some varieties of this catalyst were reported. Each of these Urushibara nickel catalysts is prepared by digesting precipitated nickel with alkali or acid. In the original preparation[3], nickel was precipitated from nickel chloride solution with zinc dust, and digested with caustic alkali to obtain U-Ni-**B**. The alternative catalyst U-Ni-A[4] was prepared by digesting the precipitated nickel with acetic acid or propionic acid instead of caustic alkali. The third catalyst U-Ni-BA[1,5] was developed by modifying the preparation of U-Ni-**B**, using aluminum grains instead of zinc dust for precipitating nickel metal from nickel chloride solution. Each of these Urushibara nickels has been found to have a comparable activity with the Raney nickel for the hydrogenation of various organic compounds.

Now it is expected that metallic cobalt and metallic copper prepared by the same procedure as to obtain the Urushibara nickel may have

1) Part VI. I. Motoyama, This Bulletin, **33**, 232 (1960).
2) K. Hata, S. Taira and T. Higase, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 186 (1957).
3) Y. Urushibara and S. Nishimura, This Bulletin, **27**, 480 (1954).
4) Y. Urushibara, S. Nishimura and H. Uehara, ibid., **28**, 446 (1955).
5) K. Hata, S. Taira and I. Motoyama, ibid., **31**, 776 (1958).

catalytic activities for hydrogenation. Actually it was already reported[6] that Urushibara cobalt B had a property similar to Raney cobalt and was recognized to be useful for the hydrogenation of nitriles. A similar copper catalyst was also reported[7] to be prepared from copper sulfate solution and zinc dust.

In case of catalytic reduction under high pressure, the reaction velocity may be influenced by various factors, namely, the nature of the groups to be reduced, the purity of substance, the activity and quantity of catalyst, the kind of solvent, the concentration and pH value of solution, the pressure of hydrogen, the temperature of reduction, the efficiency of agitation, etc. The temperature at which the absorption of hydrogen gas begins, or the time or the quantity of catalyst required for the completion of reduction, may be regarded as a measure to determine the activity of the catalyst.

In the present experiments, reduction of benzophenone is selected as an example for determining the activities of Urushibara catalysts prepared by various methods. The time required for reducing the ketone to benzhydrol was compared with each other under a similar condition.

Experimental

Apparatus. — Reductions were carried out in a Sakashita SE-20, electro-magnetically stirring type autoclave having a capacity of 200 ml.

Materials. — Benzophenone was prepared from benzoyl chloride and benzene by the Friedel-Crafts reaction[8]. The raw product was submitted to vacuum distillation and then recrystallized twice from ethanol, b. p. 140~141°C/5 mmHg, m. p. 48°C.

General Procedure for Reduction.—The catalyst containing 1 g. of nickel, cobalt, or copper was carefully transferred with ethanol into the autoclave. Then air in the autoclave was replaced by hydrogen gas. Most operations were carried out under the following conditions: (1) benzophenone; 12.74 g. (0.07 mol.) (2) ethanol(99%); 110 ml. (3) pH; 9~11 (When Urushibara catalysts A and CA were used, 0.5 ml. of 10% sodium hydroxide solution was added.) (4) agitation; 40~50 strokes per minute (5) temperature; Since a remarkable reduction of carbonyl compounds was found to begin at about 60°C as was reported in the previous paper[2], agitation was started when the temperature in the autoclave was reached at 60°C, and it was kept between 58° and 70°C. (6) Pressures were observed at intervals of five minutes.

After the reduction was finished and the autoclave got cold, hydrogen gas was discharged and the contents were taken out with ethanol. The catalyst was filtered off and washed with ethanol. The major part of the combined solvent was distilled off and the hot residue was poured into 300 ml. of hot water with stirring. The crude benzhydrol was filtered off and dried. It was recrystallized from ligroin into colorless silky needles, m. p. 68~69°C. Yield, 90~95% of the theoretical. It did not depress the m. p. with an authentic sample.

Preparation of Catalysts.—The Urushibara nickel B[3], the Urushibara nickel A[4] and the Urushibara nickel BA[1,5] were prepared by the methods described in the references cited. Some new types of Urushibara catalysts were prepared as follows. The procedures described below are the methods for the preparation of the catalysts, each containing 1 g. of catalyst metal.

(a) Urushibara Nickel B (U-Ni-B) Prepared from Nickel Acetate.—On a boiling water bath 4.24 g. of nickel acetate ($Ni(CH_3CO_2)_2 \cdot 4H_2O$) is dissolved in 20 ml. of water. This hot solution is added at once with stirring by hand onto a hot mixture of zinc dust (10 g.) and water (10 ml.) placed in a 500 ml. beaker warmed on a boiling water bath. As a vigorous reaction takes place and the reaction mixture swells up, good agitation is required to prevent the contents running over. When the reaction subsides, 200 g. of 10% sodium hydroxide solution is cautiously added with stirring onto the reaction product (precipitated nickel). The temperature of the mixture is kept at about 50~55°C for fifteen minutes with occasional stirring. When solid matter settles down, the upper liquor is decanted. The solid is washed with two 100 ml. portions of hot water, and then with two 50 ml. portions of ethanol. In this way 8.5~10.5 g. of bulky catalyst, containing nickel (about 1 g.), zinc, zinc oxide and a very small amount of alkali, is obtained.

(b) Urushibara Cobalt B (U-Co-B). — To a hot mixture (90~100°C) of zinc dust (10 g.) and water (4 ml.) placed in a 100 ml. flask is added at once 10 ml. of hot aqueous solution (90~100°C) containing 4.04 g. of cobalt chloride ($CoCl_2 \cdot 6H_2O$) with vigorous stirring on a boiling water bath. The reaction product (precipitated cobalt) is transferred into a 300 ml. beaker and washed with 200 ml. of hot water. After 160 g. of 10% sodium hydroxide solution is added, the mixture is warmed at about 50~55°C on a water bath for fifteen minutes with occasional stirring. Then the upper liquor is decanted, and the residual solid is washed with two 100 ml. portions of hot water and then with two 50 ml. portions of ethanol. About 6.5~7 g. of catalyst, containing cobalt (about 1 g.), zinc, zinc oxide and a trace of alkali, is obtained.

(c) Urushibara Nickel CB (U-Ni-CB).—Ten milliliter of aqueous solution containing 4.04 g. of nickel chloride ($NiCl_2 \cdot 6H_2O$) is added to a mixture of zinc dust (10 g.) and water (4 ml.) placed in a 100 ml. flask. This mixture is stirred at room temperature or under cooling with water or ice until the green color of nickel ion disappears. This process requires about three to four hours. As the major part of the ion exchange reaction proceeds during the initial period, the reaction mixture may be left standing until the green color has disappeared

6) S. Saito, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **76**, 351 (1956).
7) Y. Urushibara, Japanese Pat., 203309.
8) Gattermann-Wieland, "Die Praxis des organischen Chemikers", Walter de Gruyter & Co., Berlin (1940), p. 340.

after stirring for an hour. When the preparation of a large quantity of precipitated nickel is required, the reaction mixture must be cooled with ice to remove the generated heat of the reaction. The slushy precipitated nickel is transferred into a 300 ml. beaker and washed with 200 ml. of cold water. After 160 g. of cold 10% sodium hydroxide solution is added, the mixture is stirred for an hour under cooling with water or ice if necessary. When the major part of solid settles down, the upper liquor is cautiously decanted, and the solid is washed with two 100 ml. portions of cold water and then with two 50 ml. portions of ethanol. About 8~11 g. of bulky catalyst, containing nickel (about 1 g.), zinc, zinc oxide and a very small quantity of alkali, is obtained.

(d) Urushibara Cobalt CB (U-Co-CB). — This catalyst is prepared from cobalt chloride by the same procedure as is described above.

(e) Urushibara Nickel A (U-Ni-A) Prepared from Nickel Acetate.—Precipitated nickel was prepared by the same procedure as is described in (a). Instead of caustic alkali, 160 ml. of 13% acetic acid is added with stirring onto the precipitated nickel. The mixture is stirred occasionally until the generation of hydrogen gas ceases and a solid comes up to the surface of the solution which is of green color. The solid is collected on a glass filter and washed with 200 ml. of hot water and then with 100 ml. of ethanol. About 0.7 g. of catalyst, containing nickel, small quantities of zinc and zinc oxide, is obtained.

(f) Urushibara Cobalt A (U-Co-A). — The precipitated cobalt prepared by the same way as is described in (b) is treated with 160 ml. of 13% acetic acid. The mixture is stirred for about five minutes until the generation of hydrogen gas ceases and a solid comes up to the surface of the solution which is rose-colored. This coloration is necessary to obtain an active catalyst. The solid is collected on a glass filter and washed with 200 ml. of hot water and then with 100 ml. of ethanol. About 1~1.2 g. of catalyst, containing cobalt (about 0.8 g.), small quantities of zinc and zinc oxide, is obtained.

(g) Urushibara Copper (U-Cu).—To a hot mixture (90~100°C) of zinc dust (10 g.) and water (5 ml.) placed in a 200 ml. flask is added at once 10 ml. of hot aqueous solution (90~100°C) containing 2.69 g. of cupric chloride ($CuCl_2 \cdot 2H_2O$) with vigorous stirring. The reaction ends at once. The upper liquor is decanted and the solid (precipitated copper) is transferred into a 300 ml. beaker and washed with 200 ml. of hot water. After the precipitated copper is treated with 160 ml. of 13% acetic acid at 70~75°C on a water bath for about thirty minutes, the upper liquor is decanted. The solid is washed with two 100 ml. portions of hot water and then with two 50 ml. portions of ethanol. About 2~2.5 g. of black catalyst, containing copper (about 1 g.) and zinc, is obtained.

(h) Urushibara Nickel CA (U-Ni-CA).—The precipitated nickel prepared by the same way as is described in (c) is transferred into a 500 ml. beaker and is carefully treated with 200 ml. of 10% acetic acid under cooling with water. After about five minutes the generation of hydrogen gas subsides and a solid comes up to the surface of the solution, which carries more deep green color than in case of Urushibara nickel A. The solid is collected on a glass filter and washed with 200 ml. of cold water and then with 100 ml. of ethanol. About 0.6~0.8 g. of fine catalyst, containing nickel (0.4~0.5 g.), small quantities of zinc and zinc oxide, is obtained.

(i) Urushibara Cobalt CA (U-Co-CA).—This catalyst is prepared from cobalt chloride by the same way as is described above, the volume of 10% acetic acid being modified to 150 ml. for the treatment of the precipitated cobalt.

(j) Urushibara Copper C (U-Cu-C).—During ten minutes 30 ml. of cold aqueous solution containing 2.69 g. of cupric chloride is added dropwise to a vigorously stirred mixture of zinc dust (10 g.) and water (10 ml.) placed in a 100 ml. flask under cooling with ice. The precipitated copper is transferred into a 300 ml. beaker and washed with 200 ml. of cold water. After the precipitated copper is treated with 160 ml. of 13% acetic acid for two hours at room temperature, the upper liquor is decanted and the residual solid is washed with two 100 ml. portions of cold water and then with two 50 ml. portions of ethanol. About 3~4 g. of black catalyst, containing copper (about 1 g.) and zinc, is obtained. Urushibara copper catalyst carries a black color before use, and it is changed in red-brown after use for reduction.

In cases of the preparations of the Urushibara catalysts B, the Urushibara copper and the Urushibara copper C, every washing is removed by decantation. In all procedures, distilled water is used for washing, and the solid must be protected from the contact with air as far as possible after the treatment of the precipitated metals with acid or alkali.

Results and Discussion

The results obtained from the reduction of benzophenone which was purified by a single vacuum distillation are summarized in Tables I and II. A series of experiments shown in Table I were carried out to examine the effect of initial pressure, and to find the difference due to the kind of nickel salt or amount of zinc dust used for preparing the catalyst. The activities of U-Ni-B and U-Co-B were also compared. As seen from Table I, the velocity of reduction was affected only slightly, if any, by the initial pressure within 30~134 kg./cm^2. Therefore the effect of the initial pressure was ignored in the following operations. The use of potassium hydroxide solution for digesting the precipitated nickel in place of sodium hydroxide solution gave the similar result (Exp. No. 14). The U-Ni-B contains a large quantities of zinc and zinc oxide aside from nickel metal. To diminish these ingredients the precipitated nickel was prepared with less amount of zinc dust and was treated with much quantities of alkaline solution (Exp. No. 15). As the catalyst thus obtained was less active and the velocity of reduction was depressed in the course of the

TABLE I. REDUCTION OF BENZOPHENONE* WITH U-Ni-B OR U-Co-B

Exp. No.	Catalyst[a)]	pH	Total weight of catalyst g.[b)]	Initial press. kg./cm²	Initial temp., °C	React. temp. °C	Time min.
11	U-Ni-B	10.2		40	20	58~65	95
12	U-Ni-B	11.1		134	22	58~67	95
13	U-Ni-B	8.9	6.7	30	29	58~67	95
14	U-Ni-B[c)]	8.3		50	26	58~64	100
15	U-Ni-B[d)]	11		50	17	59~76	165
16	U-Ni-B[e)]	10.8	9.5	45.5	20	58~66	55
17	U-Ni-B[e)]	11.3		35	23	58~64	55
18	U-Ni-B[e,f)]	10.6	9	65	25	58~66	65
19	U-Co-B	10.1		55	26	58~68	95

* Benzophenone, purified by a single vacuum distillation, was used.
a) Each catalyst was prepared so as to contain 1 g. of nickel or cobalt.
b) The figures were obtained by weighing the dried catalysts after use for reduction.
c) The precipitated nickel was treated with 200 g. of 14% potassium hydroxide solution.
d) The precipitated nickel, obtained from nickel chloride solution with 5 g. of zinc dust, was treated with two 150 g. portions of 10% sodium hydroxide solution.
e) The precipitated nickel was prepared from nickel acetate. The other was prepared from nickel chloride.
f) The precipitated nickel was treated with 150 g. of 20% sodium hydroxide solution.

reaction, higher temperature was required to complete the reaction. This may be partly due to the big size of the particles of nickel metal and partly to the contact with an alkali for a long time. Moreover, it must be considered that the zinc and zinc oxide contaminated in the U-Ni-B may act as carrier[9]. For the reduction of benzophenone, purified by a single vacuum distillation, the U-Ni-B prepared from nickel acetate was more effective than the catalyst obtained from nickel chloride (Exp. Nos. 16, 17, 18), but this was not always true, when more carefully purified benzophenone was used. The U-Ni-B prepared from nickel acetate weighs in dry state about 8.5~10.5 g. (for 1 g. of nickel), and is about three times as bulky as the catalyst obtained from nickel chloride. Therefore, it must contain more zinc oxide (cf. micro-photograph, Fig. 1 (d)), which may act as a sort of an effective carrier in the reduction of a less purified substance.

It was already reported[10], that the catalytic reduction of a carbonyl group with Raney nickel was accelerated by a trace of alkali. For the Urushibara nickel catalyst, the effect of an alkali was quantitatively investigated in the reduction of cyclohexanone under ordinary pressure[11]. The results of the reduction of benzophenone in neutral solution with the Urushibara catalyst A and the well washed Urushibara catalyst B are shown in Table II. From these results, it is obvious that the catalytic reduction of a carbonyl group with these catalyst is desirable to operate above pH 8 (S. Nishimura reported that the excess of alkali retarded the reaction[11]).

The results tabulated in Tables III, IV, V and VI were obtained by the use of more carefully purified benzophenone, which was recrystallized twice from ethanol after vacuum distillation. The effect of purification was remarkable when the U-Ni-B was used. The U-Ni-BA was reported to be specially useful in the hydrogenation of aromatic nucleus[1,5], but it was found to be not so particularly effective for the reduction of a carbonyl group (Table III, Exp. Nos. 37, 38). It was revealed by micro-photographs that the size of the particles of the U-Ni-BA catalyst is greater than that of the other Urushibara catalysts* as shown in Fig. 1. Also the X-ray diffraction of the U-Ni-BA gives a different pattern from that of the U-Ni-A. The U-Co-BA was proved to be less active for the reduction of benzophenone, and it required higher temperature and longer time to finish the reduction than the other Urushibara catalysts (Exp. No. 39). As was already described, the U-Ni-A in neutral solution was not suitable for the reduction of a carbonyl group. But an addition of a small amount of alkali promoted remarkably the reduction and such a nickel catalyst gave better results than those obtained with the U-Ni-B (Exp. Nos. 310—313). The reason may be partly supposed to be due to the dispersability of the catalyst.

9) Y. Urushibara, S. Yamaguchi and M. Kobayashi, This Bulletin, 29, 816 (1956).
10) M. Delépine and A. Horeau, *Bull. soc. chim. France*, [5] 4, 31 (1937).
11) S. Nishimura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 79, 56 (1958).
* The size of the particles of Urushibara copper catalyst is as large as that of the U-Ni-BA.

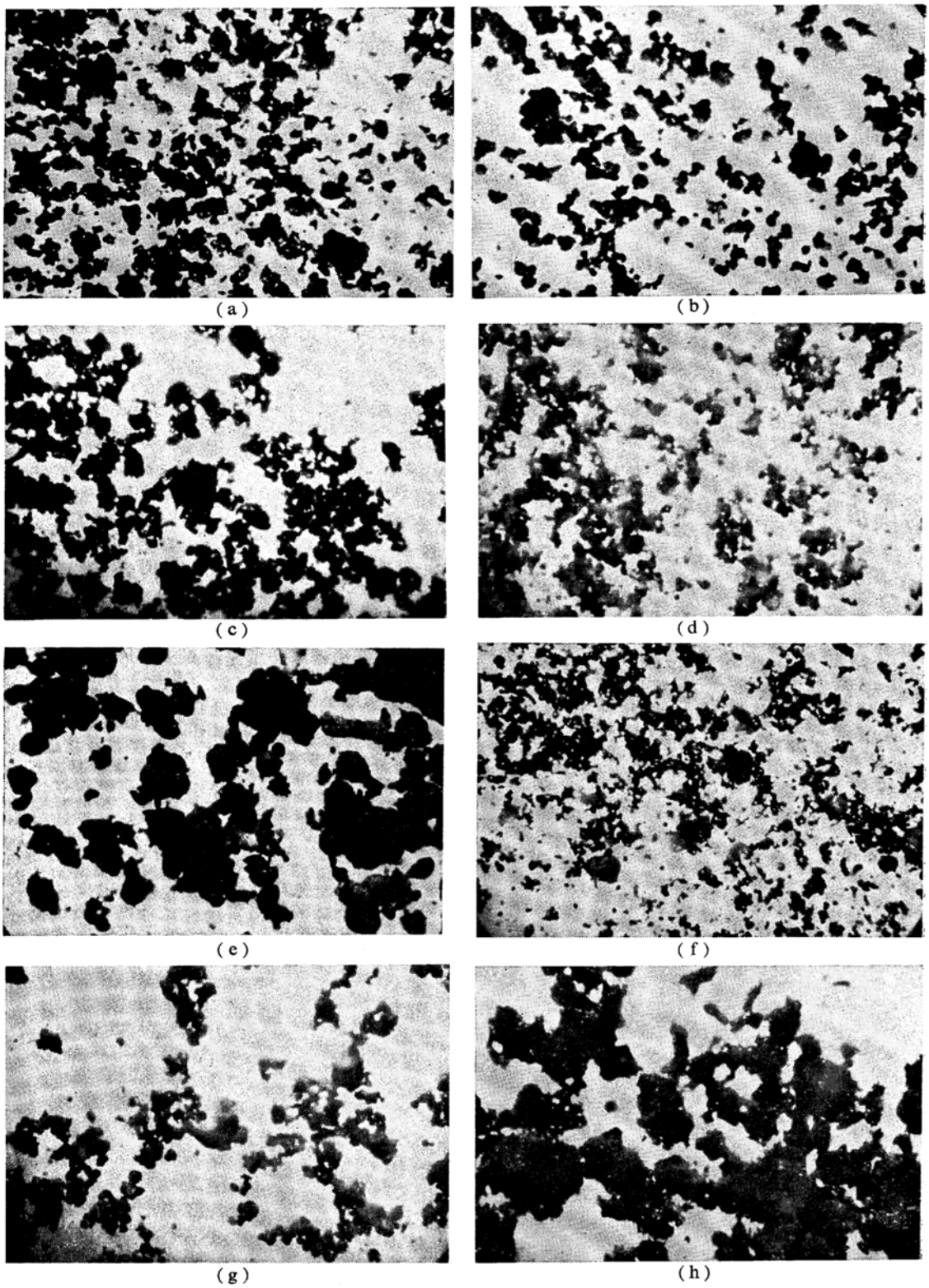

Fig. 1. Micro-photographs of Urushibara catalysts (×150).
(a) U-Ni-A (b) U-Ni-B (c) U-Ni-A (The precipitated nickel was prepared from nickel acetate.) (d) U-Ni-B (The precipitated nickel was prepared from nickel acetate.) (e) U-Ni-BA (f) U-Co-A (g) U-Co-B (h) U-Cu.

TABLE II. REDUCTION IN NEUTRAL SOLUTION

Exp. No.	Catalyst[a]	pH	Total weight of catalyst g.[b]	Initial press. kg./cm²	Initial temp., °C	React. temp. °C	Time min.
21	U-Ni-B[c,d]	7.5		45	20	58～ 66	250
22	U-Co-B[d]	7.7	6.6	55	22	58～ 66	165
23	U-Ni-A	7		55	22	58～ 64	155
24	U-Ni-A[c]	6.8	0.7	45	18	62～102	205
25	U-Co-A	6.7		50	20	62～ 76	180

Benzophenone, purified by a single vacuum distillation, was used.

a) Each catalyst was prepared so as to contain 1 g. of nickel or cobalt.
b) The figures were obtained by weighing the dried catalysts after use for reduction.
c) The precipitated nickel was prepared from nickel acetate instead of nickel chloride.
d) The catalysts were thoroughly washed with water to remove a trace of alkali.

TABLE III. REDUCTION OF CAREFULLY PURIFIED BENZOPHENONE*

Exp. No.	Catalyst[a]	pH	Total weight of catalyst g.[b]	Initial press. kg./cm²	Initial temp., °C	React. temp. °C	Time min.
31	U-Ni-B	9.7	6.5	30	24	58～68	75
32	U-Ni-B	9.3	6.8	49.5	22	63～67	25
33	U-Ni-B	9.4	6.6	52.5	28	61～66	35
34	U-Ni-B[c]	11.1	11.2	50	16	63～66	30
35	U-Co-B	10.4	7	50	15	60～69	70
36	U-Co-B	9	6.2	56	24	61～65	65
37	U-Ni-BA	10.5	1.4	50	15	60～64	45
38	U-Ni-BA	10.6	1.8	45	14	62～66	35
39	U-Co-BA	10.2	0.8	45	16	72～84	115
310	U-Ni-A	10.5[d]	1.1[e]	52	25	60～63	10
311	U-Ni-A	10.3[d]	1.4[e]	46	26	59～62	8
312	U-Ni-A	10.1[d]	1.4[e]	48.5	20	59～63	6
313	U-Ni-A	10[d]	1.3[e]	46	29	60～62	12
314	U-Ni-A[c]	10.4[d]	0.7	45	24	59～66	60
315	U-Co-A	10.1[d]	1[e]	45	22	61～66	45
316	U-Co-A	10.4[d]	1.2[e]	49.5	25	59～65	50

* Benzophenone, purified by a single vacuum distillation and then recrystallized twice from ethanol, was used.

a) Each catalyst was prepared so as to contain 1 g. of nickel or cobalt.
b) The figures were obtained by weighing the dried catalysts after use for reduction.
c) The precipitated nickel was prepared from nickel acetate. The other was prepared from nickel chloride.
d) 0.5 ml. of 10% sodium hydroxide solution was added.
e) The quantities of nickel or cobalt were about 0.75～0.85 g.

TABLE IV. REDUCTION WITH THE U-Ni-A OF LOW ACTIVITY

Exp. No.	Weight of cat., g.[a]	pH[b]	Weight of sample, g.	Volume of ethanol ml.	Initial press. kg./cm²	Initial temp. °C	React. temp. °C	Time min.
41	1	10.7	12.74	110	45	16	60～ 66	30
42	2	10	12.74	110	40	22	62～ 66	10
43	1	10.1	12.74	55	32	20	60～ 68	10
44	1	10.2	25.48	110	60	14	61～ 66	20
45	1	10.2	12.74	110	50	20	97～100[c]	7
46	1	10.5	12.74	55	45	18	98～108[c]	4

Benzophenone, purified by a single vacuum distillation and then recrystallized twice from ethanol, was used.

a) The figures are weight of nickel metal to be included in catalysts.
b) 0.5 ml. of 10% sodium hydroxide solution was added.
c) The time for heating the autoclave before starting agitation was equal to those of the other experiments.

TABLE V. REDUCTION WITH URUSHIBARA CATALYSTS C

Exp. No.	Catalyst[a]	pH	Total weight of catalyst g.[b]	Initial press. kg./cm²	Initial temp., °C	React. temp. °C	Time min.
51	U-Ni-CB[c]		5.7	34.5	16	62~65	35
52	U-Ni-CB[c]	10.2	11.5	56	22	60~62	20
53	U-Ni-CB[d]	10.7	8.8	60	25	60~66	15
54	U-Ni-CB[d]	10	9.6	50	22	68~70	10
55	U-Ni-CA[c]	10.1[e]	0.55	40	14	66~70	15
56	U-Ni-CA[c]	10.5[e]	0.55	42	13	62~66	10
57	U-Ni-CA[c]	10.3[e]	0.7	50	17	63~65	20
58	U-Ni-CA[c]	10[e]	0.7	50	20	60~63	15
59	U-Ni-CA[c]	10[e]		60	26	61~65	10
510	U-Ni-CA[d]	10.2[e]	0.6	52.5	20	62~64	10
511	U-Ni-CA[d]	9.8[e]	0.5	42.5	24	58~60	30
512	U-Ni-CA[d]	10[e]		55	24	62~66	15
513	U-Co-CB[c]	10.5	8.5	60	20	60~62	35
514	U-Co-CB[c]	10.5	7.8	40	23	59~60	35
515	U-Co-CB[d]	10.6	3.4[f]	60	20	62~66	35
516	U-Co-CB[d]	10.2	3.2[f]	52	28	60~66	35
517	U-Co-CA[c]	10.7[e]	1.1	55	22	60~64	30
518	U-Co-CA[d]	10.6[e]	1.4	55.5	23	60~62	60[g]
519	U-Co-CA[c]	10.4[e]	1.4	37	22	59~62	80[g]

Benzophenone, purified by a single vacuum distillation and then recrystallized twice from ethanol, was used.

a) Each catalyst was prepared so as to contain 1 g. of nickel or cobalt.
b) The figures were obtained by weighing the dried catalysts after use for reduction.
c) The precipitated metal was prepared at room temperature.
d) The precipitated metal was prepared under cooling with ice.
e) 0.5 ml. of 10% sodium hydroxide solution was added.
f) The precipitated cobalt was digested for 1.5 hr. under cooling with ice.
g) The major part of the catalyst proved to be deposited on the flange of copper packing after the reduction was finished. The reason was not clear, but the magnetic nature of this catalyst might be different from the other catalysts.

TABLE VI. REDUCTION WITH URUSHIBARA COPPER CATALYST

Exp. No.	Catalyst[a]	pH[b]	Total weight of catalyst g.[c]	Initial press. kg./cm²	Initial temp., °C	React. temp. °C	Time min.
61	U-Cu	10	2.2	40	16	100~118	40
62	U-Cu	9.5	2.4	53	24	110~120	65
63	U-Cu-C	10.3	4.2	50	28	110	10
64	U-Cu-C		2.8	52.5	22	120~121	15

Benzophenone, purified by a single vacuum distillation and then recrystallized twice from ethanol, was used.

As a solvent 55 ml. of ethanol was used.

a) Each catalyst was prepared so as to contain 1 g. of copper.
b) 0.5 ml. of 10% sodium hydroxide solution was added.
c) The figures were obtained by weighing the dried catalyst after use for reduction.

As the apparent bulk of the U-Ni-A is much smaller than that of the U-Ni-B, the fine particles of the former may be easily dispersed into a solution by the up and down agitation employed in these experiments. However, the U-Ni-A prepared from nickel acetate was less active than the U-Ni-B prepared from the same salt (Exp. No. 314), and the reason is obscure. In alkaline solution the U-Co-A also gave better results than those obtained with the U-Co-B (Exp. Nos. 315, 316).

Reaction temperature, concentration of solution and quantity of catalyst are naturally expected to exert some influences on the rate of reduction. As a catalyst with high activity is not suitable for the purpose of this series of experiments, the U-Ni-A, which was specially prepared to have a lower activity, was used.

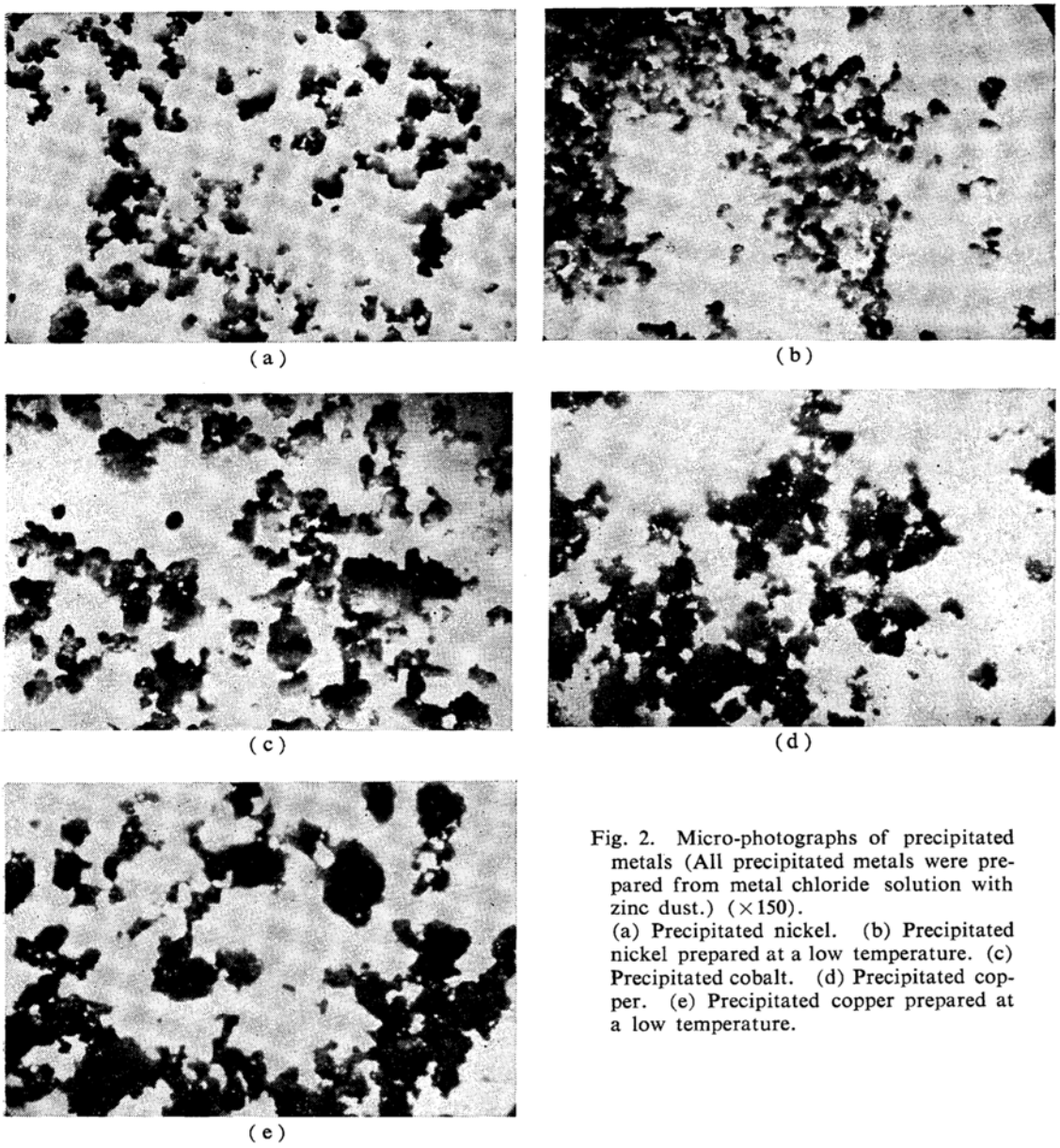

Fig. 2. Micro-photographs of precipitated metals (All precipitated metals were prepared from metal chloride solution with zinc dust.) (×150).
(a) Precipitated nickel. (b) Precipitated nickel prepared at a low temperature. (c) Precipitated cobalt. (d) Precipitated copper. (e) Precipitated copper prepared at a low temperature.

The results are listed in Table IV. To obtain a highly active U-Ni-A, the treatment of the precipitated nickel with diluted acetic acid should be continued until the solution acquires the green color of nickel ion. The U-Ni-A, used for these experiments, was prepared by interrupting the digestion before the solution was colored. The activity of this catalyst was considerably lower than that of the ordinary U-Ni-A. As shown in Table IV, the increment of either the concentration of solution or the amount of catalyst exerts a similar favorable effect on the reduction of benzophenone.

The first step of the preparation of Urushibara catalyst is to obtain precipitated metal by an ion exchange reaction. The so-called precipitated metal may consist of particles of metallic zinc covered with proper metal to be used as a catalyst, admixed with a quantity of zinc dust and zinc compounds. It can be said that the former is a true precipitated metal. Supposing that the size of the particles of a catalyst are decided mainly by those of the precipitated metal, it is necessary to prepare the fine particles of the precipitated metal for making the particles of catalyst to be fine. When a definite weight of zinc dust is used for preparing a definite weight of catalyst, the size of the particles of the precipitated metal may be decided by the size of the particles of

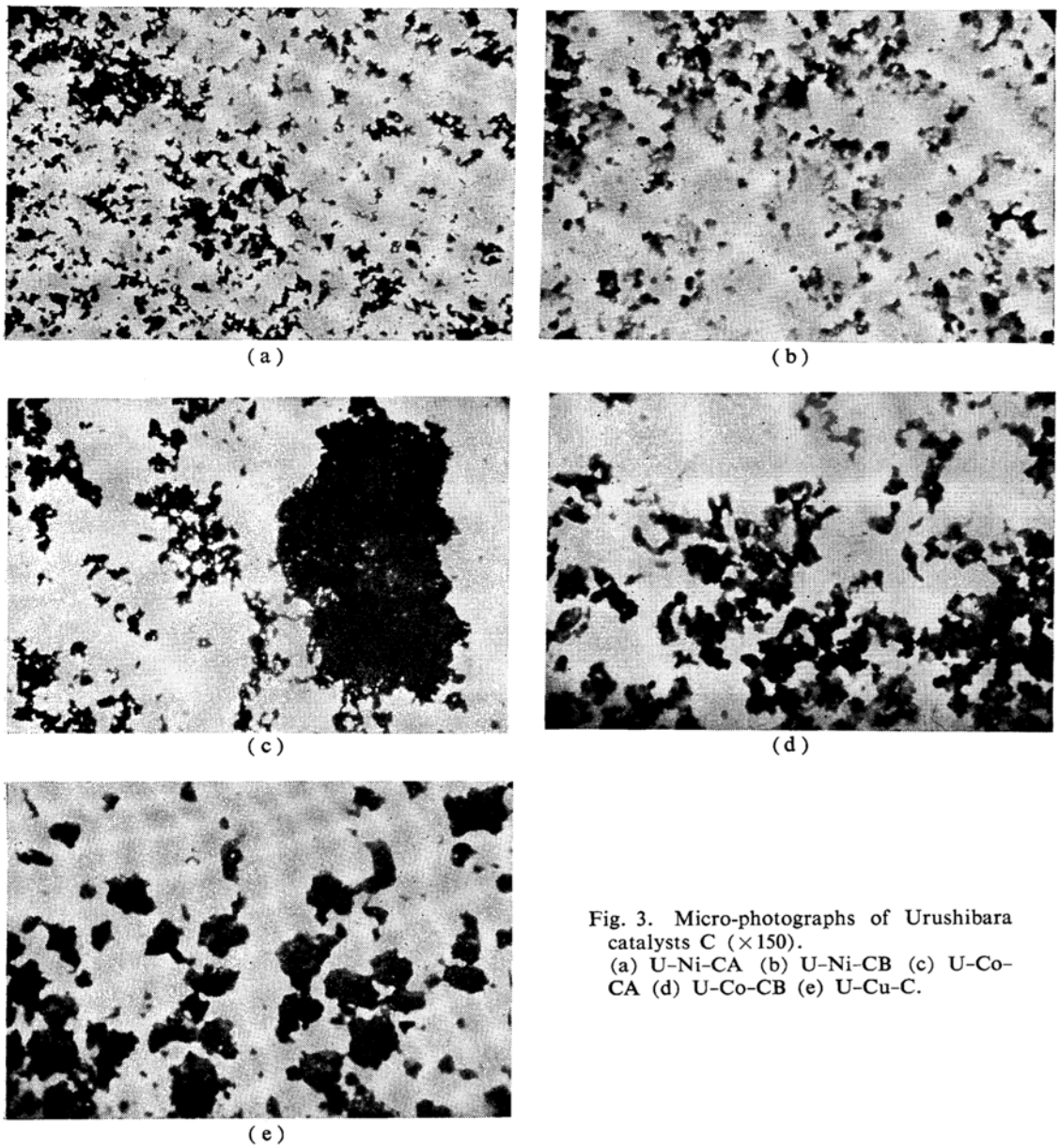

Fig. 3. Micro-photographs of Urushibara catalysts C (×150).
(a) U-Ni-CA (b) U-Ni-CB (c) U-Co-CA (d) U-Co-CB (e) U-Cu-C.

zinc dust and the rate of the ion exchange reaction. The rate of the ion exchange reaction may be affected by several factors, such as the difference of the standard electrode potential between zinc and the metal used to form a catalyst, the fineness of zinc dust, the concentration of the solution of metal chloride, the temperature and the efficiency of agitation when the precipitated metal is prepared. Of the above-mentioned factors, the size of the particles of zinc dust is difficult to change, so far as a commercially available product is used. The difference of the standard electrode potential is almost constant, and the improvement of the efficiency of agitation is limited to some extent. If the concentration of the solution of metal chloride is definite, only the temperature at which the ion exchange reaction is carried out can be freely varied. At a low temperature the ion exchange reaction occurs very slowly, and the influence of the efficiency of agitation can be minimized. Consequently, the metal may uniformly separate out on the surface of the particles of zinc dust and then fine particles of catalyst may be obtained (cf. micro-photographs, shown in Fig. 2).

Urushibara catalysts, thus prepared at a low temperature as described in the experimental part, are temporarily named Urushibara catalysts C and the abbreviations, such as U-Ni-CB,

U-Ni-CA, etc., are used. The results obtained with these catalysts are shown in Table V.

With the U-Ni-CB, better results were obtained than with the U-Ni-B. The dried U-Ni-CB is somewhat heavier in weight and more bulky than the U-Ni-B. The appearance of the U-Ni-CB resembles that of the U-Ni-B prepared from nickel acetate. A microphotograph (Fig. 3) shows that the size of the particles of this catalyst are somewhat smaller than that of the U-Ni-B, and that much zinc oxide remains undissolved. The U-Ni-CA was also proved to be effective, but somewhat longer time was necessary with this catalyst to finish the reduction than with the U-Ni-A. It is partly explained by the fact that the weight of the U-Ni-CA is about a half of that of the U-Ni-A. In the same manner, the U-Co-CB and the U-Co-CA were found to be superior to the corresponding ordinary cobalt catalyst.

To obtain a highly active Urushibara catalyst it has been claimed that the ion exchange reaction to obtain the precipitated metal should be carried out in a short time at a high temperature. Nevertheless, it was proved as mentioned above that the precipitated metal prepared in a long time at a low temperature gives an excellent catalyst. The X-ray diffraction of the U-Ni-CA gives a somewhat different pattern from that of the U-Ni-A, and it will be reported in another paper.

In Table VI the results obtained with copper catalyst are shown. As the precipitated copper does not react with 10% sodium hydroxide solution, only acid is a suitable reagent for treating the precipitated copper. The copper catalyst being considered not so active as a nickel catalyst for catalytic reduction, the condition of reduction was decided in consideration of the results obtained in Table IV. The results shown in Table VI are similar to those obtained with Raney copper[12]. Again, the U-Cu-C gave better results than those obtained with the ordinary U-Cu.

Summary

High pressure reduction of benzophenone was examined with various Urushibara catalysts under various conditions. The purity of benzophenone, the concentration and pH of a solution, reaction temperature and quantity of the catalyst exerted considerable effects on the rate of reduction. Effective Urushibara catalysts were prepared from the precipitated metals which were obtained from the metal chlorides and zinc dust at a low temperature.

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