Reduction of Organic Compounds with Urushibara Catalysts under High Pressure. VIII⁽¹⁾*. Reduction of Acetophenone, Especially with Urushibara Nickel Catalyst Prepared by Various Modified Methods*

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In the preceding paper[1] of this series, catalytic reduction of benzophenone with various Urushibara catalysts under various conditions was reported, and activities of Urushibara nickel, Urushibara cobalt and Urushibara copper, prepared by various methods were compared with each other.

The procedure for preparing Urushibara nickel catalyst has been successively modified since its discovery and some varieties of this catalyst were reported. The preparation of the Urushibara nickel catalyst is divided into two steps; namely, the preparation of precipitated nickel and the digestion of the precipitated nickel with acid or alkali. Varieties of the Urushibara nickel catalyst originate in methods of preparing the precipitated nickel and succesive treatment with acid or alkali. The precipitated nickel, prepared from nickel chloride or nickel acetate solution with zinc dust, gives Urushibara nickel B (U-Ni-B)[1,2] or Urushibara nickel CB (U-Ni-CB)[1] by digestion with caustic alkali. The same precipitated nickel gives Urushibara nickel A (U-Ni-A)[1,3] or Urushibara nickel CA (U-Ni-CA)[1] by treatment with acetic acid in place of caustic alkali. The U-Ni-CB and U-Ni-CA are prepared from the precipitated nickel which was obtained from nickel chloride solution and zinc dust at a low temperature. The precipitated nickel, prepared from nickel chloride solution with aluminum grains, gives Urushibara nickel BA (U-Ni-BA)[4,5] by treatment with sodium hydroxide solution, and Urushibara nickel AA (U-Ni-AA)[6] by treatment with acetic acid and sodium chloride.

In the present paper, reduction of acetophenone with various Urushibara nickel catalysts is investigated. In this connection, the possibility of preservation of the precipitated nickel retaining the activity of the catalyst therefrom was examined. The renewal of used catalyst was also examined, and it was found that a highly active catalyst can be regenerated from a used catalyst by a simple procedure.

Experimental

Apparatus.—Reduction was carried out in the same autoclave (Sakashita SE-20; electro-magnetically stirring type autoclave having a capacity of 200 ml.) used in the experiments reported in the preceding paper[1].

Materials.—Commercially available acetophenone was purified by repeated crystallization.

General Procedure for Reduction.—Any catalyst, prepared so as to contain 1 g. of nickel, was carefully transferred with ethanol into the autoclave. Then the air present in the autoclave was replaced

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[1] Part VII: S. Taira, This Bulletin, 34, 261 (1961).

[2] Y. Urushibara and S. Nishimura, ibid., 27, 480 (1954).

[3] Y. Urushibara, S. Nishimura and H. Uehara, ibid., 28, 446 (1955).

[4] K. Hata, S. Taira and I. Motoyama, ibid., 31, 776 (1958).

[5] I. Motoyama, ibid., 33, 232 (1960).

[6] K. Hata, K. Watanabe and H. Watanabe, ibid., 32, 6 (1959).

by hydrogen gas four times. All operations were carried out under the following condition: (1) acetophenone: 30 g. (0.25 mol.), (2) ethanol: 60 ml., (3) pH: 9∼11 (It has been recognized[1,7,8] that the catalytic reduction of carbonyl group with Urushibara catalyst was accelerated by a trace of alkali. When U-Ni-A or U-Ni-CA was used, 1 ml. of 10% sodium hydroxide solution was added.), (4) agitation: 40∼45 strokes per minute, (5) reaction temperature: as a remarkable hydrogen uptake was found to begin at about 60°C in reduction of carbonyl group[7], agitation was started when the temperature in the autoclave reached about 60°C, and the temperature was kept between 60 and 70°C throughout the operation, (6) pressure: as it had been found that, in the case of the reduction of carbonyl group under high pressure, the velocity of reduction was only slightly affected by the initial pressure under 100 kg./cm^2 [1,7], the effect of the initial pressure was ignored and (7) when the pressure in the autoclave dropped to 20∼30 kg./cm^2, supplementary hydrogen gas was charged two or three times in every course of the operation, and the reduction was continued until the hydrogen uptake ceased. Pressure was observed at intervals of five minutes.

After the reduction was finished, the catalyst was filtered off and washed with ethanol. From the combined filtrate, the major part of the ethanol was removed by distillation on a water bath, and the residual liquid was distilled under reduced pressure. The fraction, distilling at 89∼91°C/15 mmHg, was collected. The yield of methylphenylcarbinol was 91∼95 per cent of the theoretical amount.

Preparation of Catalysts. — The U-Ni-B[1,2], U-Ni-CB[1], U-Ni-BA[4,5], U-Ni-A[3] and U-Ni-CA[1] were prepared by the methods described in the references cited. Regenerated Urushibara nickel catalyst was prepared from any used catalyst by the following methods. The used catalyst was recovered by filtration after the previous reaction, and dried at about 100°C and stored.

(A) To well-mixed zinc dust (5 g.) and recovered U-Ni-A (1.3 g.) with water (3 ml.) was added 80 g. of 10% sodium hydroxide solution. The mixture was occasionally stirred for 20 min. at 50∼55°C and then 5 min. at 75∼80°C. At the end of this process, generation of hydrogen gas ceased and grayish white zinc compounds were deposited. The upper liquor was removed by decantation and the residual solid was washed with 200 ml. of hot water and then with two 50 ml. portions of ethanol. Every washing was decanted.

(B) Recovered U-Ni-A (1.3 g.), used in Exp. No. 113 and left standing for 55 days, was well mixed with zinc dust (10 g.) and water (5 ml.). The mixture was treated with 160 g. of 13% acetic acid for about 5 min. As hydrogen gas was vigorously generated at first, good agitation by hand was required to prevent the contents from running over. In this case the solid did not come up to the surface of the solution which was green in color. The solid was collected on a glass filter and washed with 200 ml. of water and then with 100 ml. of ethanol.

(C) To a mixture of the recovered U-Ni-A (1.1 g.) used in Exp. No. 32, zinc dust (5 g.) and water (3 ml.) was added 80 g. of 13% acetic acid. The following procedure was similar to that described in B, and a very fine catalyst was obtained.

(D) To a mixture of recovered U-Ni-A (1.4 g.), zinc dust (2.5 g.) and water (2.5 ml.) was added 40 g. of 13% acetic acid. The following procedure was similar to that described in B.

(E) The recovered U-Ni-B (7.3 g.) used in Exp. No. 11 was treated with 160 g. of 13% acetic acid until the solid came up to the surface of the solution which had turned green. Since the major part of the zinc dust had been removed in the previous preparation of the U-Ni-B, only a small quantity of hydrogen gas was evolved in this process. The solid was collected on a glass filter, and washed with 200 ml. of water and then with 100 ml. of ethanol.

(F) The recovered U-Ni-CB (7 g.) used in Exp. No. 19 was treated with 160 g. of 13% acetic acid. Generation of hydrogen gas was hardly observed, and the solution turned black owing to the suspension of fine solid. After about 8 min. the solid was separated by centrifuge from the solution which was green in color. The solid was washed with two 200 ml. portions of water and then two 50 ml. portions of ethanol in the centrifugal tube. The washings were decanted.

(G) To a mixture of recovered U-Ni-A (1.4 g.) and water (2 ml.) was added 50 g. of 20% acetic acid. The mixture was then digested at 70∼75°C for one minute on a boiling water bath. The U-Ni-A reacted vigorously with acetic acid at this temperature. Then solid, adsorbing hydrogen gas, came up to the surface of the solution which was green in color. The solid was collected on a glass filter and washed with 200 ml. of water and then with 100 ml. of ethanol.

(H) The weight of recovered U-Ni-A, prepared so as to contain 1 g. of nickel, being ordinary 1.3 ∼1.4 g., the recovered U-Ni-A (0.9 g.) used in Exp. No. 37 was supplemented by 0.5 g. of recovered and stored U-Ni-A. To this was added 2 ml. of water and the mixture was treated as is described in G.

(I) To a mixture of recovered U-Ni-A (1.4 g.) and water (2 ml.) was added 50 g. of 10% acetic acid. The mixture was digested at 75∼80°C for one minute on a water bath. The following procedure was similar to that described in G.

In all procedures, distilled water was used for washing, and the obtained catalyst was protected from contact with air as far as possible.

Results and Discussion

As reported in the preceding paper[1] on the reduction of benzophenone, the activity of various Urushibara nickel catalysts in the reduction of acetophenone was studied by comparing the time required for the completion

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[7] K. Hata, S. Taira and T. Higase, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 186 (1957).

[8] S. Nishimura, ibid., **79**, 56 (1958).

TABLE I. REDUCTION OF ACETOPHENONE WITH VARIOUS URUSHIBARA NICKEL CATALYSTS

Exp. No.	Catalyst[a]	pH	Total weight of catalyst g.[b]	Initial pressure kg./cm²	Total pressure depression kg./cm²[c]	Initial temp. °C	Reaction temp. °C	Time min.
11	U-Ni-B	10	7.3	45	56.5	22	61~70	125
12	U-Ni-B	9.7	8.6	50	54.5	23	60~70	90
13	U-Ni-B	9.3	7.4	47	57	22	61~70	80
14	U-Ni-B	9	7.5	46	52	21	62~70	70
15	U-Ni-B[d]	10.6	10.5	42	59	25	62~70	105
16	U-Ni-B[d]	10.5	10.8	45	55	21	60~70	105
17	U-Ni-BA	9.4	1.2	40.5	51	25	61~70	120
18	U-Ni-BA	10.4	1.1	45	50	23	62~70	95
19	U-Ni-CB	9.7	7	49.5	56.5	22	63~66	65
110	U-Ni-CB	10.4	9.2	50	63	21	61~66	60
111	U-Ni-CB	10.7	8.4	49	71	30	64~69	50
112	U-Ni-A	9.5[e]	1.3	47	54.5	24	60~68	40
113	U-Ni-A	10[e]	1.3[f]	45	51.5	24	60~68	35
114	U-Ni-A	9.8[e]	1.3	46	50	24	61~68	35
115	U-Ni-A	9.2[e]	1.3[f]	49	55.5	24	62~70	25
116	U-Ni-CA	9.5[e]	0.9[g]	42	49.5	20	62~69	50
117	U-Ni-CA	9.6[e]	0.8[g]	47.5	55.5	20	62~66	50
118	U-Ni-CA	9.4[e]	0.6	49	51	17	65~70	40
119	U-Ni-CA	9.4[e]	0.7	44	46.5	22	61~69	40

a) Each catalyst was prepared so as to contain 1 g. of nickel.
b) The figures were obtained by weighing the recovered and dried catalysts.
c) Supplementary hydrogen gas was charged two or three times in course of the operation. Every depression of the pressure was sumed up.
d) The catalyst was prepared from the precipitated nickel, obtained from nickel acetate solution and zinc dust.
e) 1 ml. of 10% sodium hydroxide solution was added.
f) About 0.83 g. of nickel was found to be contained by analysis.
g) About 0.57 g. of nickel was found to be contained by analysis.

TABLE II. REDUCTION OF ACETOPHENONE WITH URUSHIBARA NICKEL CATALYSTS PREPARED FROM PRESERVED PRECIPITATED NICKEL[a]

Exp. No.	Catalyst[b]	pH	Total weight of catalyst g.[c]	Initial pressure kg./cm²	Total pressure depression kg./cm²[d]	Initial temp. °C	Reaction temp. °C	Time min.
21	U-Ni-B	9.2	9	48	57	32	60~69	85
22	U-Ni-B	9.3	8.6	47	55	24	60~68	50
23	U-Ni-A	9.4[e]	1.2	48	53.5	27	60~68	35
24	U-Ni-A	9.7[e]	1.3	50	52.5	25	61~65	40

a) All catalysts were prepared from precipitated nickel, obtained from nickel chloride solution and zinc dust, washed with water, dried at about 100°C and left standing for a week in the air.
b) Each catalyst was prepared so as to contain 1 g. of nickel.
c) The figures were obtained by weighing the recovered and dried catalysts.
d) Supplementary hydrogen gas was charged twice in course of the operation. Every depression of the pressure was sumed up.
e) 1 ml. of 10% sodium hydroxide solution was added.

of reduction under nearly the same condition.

A series of experiments shown in Table I was carried out to confirm the activity of each catalyst and to offer the standard of reference for the subsequent experiments. The reduction of acetophenone was effectively achieved with U-Ni-B, U-Ni-BA, U-Ni-CB, U-Ni-A and U-Ni-CA, among which U-Ni-A proved to be the most useful. The U-Ni-B, prepared from nickel acetate and zinc dust, which had been found to be similarly active in the reduction of benzophenone, was also effective for the reduction of acetophenone though somewhat less active (Exp. Nos. 15 and 16). The U-Ni-BA, which had been proved to be specially useful for hydrogenation of aromatic nucleus[4,5], was not so particularly active (Exp. Nos. 17 and 18) as it was in the reduction of

TABLE III. REDUCTION OF ACETOPHENONE WITH REGENERATED URUSHIBARA NICKEL CATALYSTS

Exp. No.	Catalyst (regenerated)	Original catalyst	Method of regeneration[a]	Total weight of catalyst g.[b]	Initial press. kg./cm^2	Total press. depression kg./cm^2 [c]	Initial temp. °C	Reaction temp. °C	Time min.
31	U-Ni-B	U-Ni-A	A	5.7	49.5	59	21	60∼64	130
32	U-Ni-A	U-Ni-A	B	1.1	50.5	50	14	65∼69	30
33	U-Ni-A	U-Ni-A	C	0.9[d]	45.5	51.5	20	61∼64	45
34	U-Ni-A	U-Ni-A	D	1.1	47	52	18	60∼64	40
35	U-Ni-A	U-Ni-B	E	1.1[e]	46	55.5	21	60∼68	45
36	U-Ni-A	U-Ni-CB	F	0.8[d]	46.5	52.5	26	63∼69	60
37	U-Ni-A	U-Ni-A	G	0.9	47.5	55.5	26	60∼64	40
38	U-Ni-A	U-Ni-A	H	0.9	48	55.5	22	61∼63	40
39	U-Ni-A	U-Ni-A	I	0.8	48.5	54.5	20	60∼65	45

In all operations excepting Exp. No. 31, 1 ml. of 10% sodium hydroxide solution was added.

a) The marks A, B, C and etc. indicate the paragraphs in Experimental part.

b) The figures were obtained by weighing the recovered and dried catalysts.

c) Supplementary hydrogen gas was charged twice in course of the operation. Every depression of the pressure was sumed up.

d) About 0.5 g. of nickel was found to be contained by analysis.

e) About 0.7 g. of nickel was found to be contained by analysis.

benzophenone[1]. The activities of U-Ni-CB and U-Ni-CA were found to be fairly high, though they were somewhat inferior to that of U-Ni-A.

The usual Urushibara nickel catalysts B and A can be prepared by a simple operation in only one hour or less. Supposing the relation of the precipitated nickel to Urushibara nickel catalyst is similar to that of Raney alloy to Raney nickel catalyst, the operation of preparing Urushibara nickel catalyst is certainly more simplified when precipitated nickel can be stored in the state ready to use. It has been claimed that precipitated nickel is inherently provided with active nickel surfaces and acid or alkali is not effective to create any active state on the surfaces, and that the rôle of acid or alkali is to remove the basic zinc chloride which has been formed by the reaction of zinc dust with nickel chloride solution[3]. It is presumable in this view that exposure of precipitated nickel to air for a long time may cause the deactivation or lowering of activity of the catalyst prepared from it. Some experiments on the preservation of precipitated nickel have already been reported in regard to the preparation of U-Ni-BA[5]. Precipitated nickel prepared from nickel chloride solution with aluminum grains was preserved in distilled water, 99% ethanol or dry state under reduced pressure. The U-Ni-BA, prepared from the preserved precipitated nickel, was unexpectedly shown to have practically the same activity as that which the catalyst prepared from freshly prepared precipitated nickel has.

The present author tried reduction of acetophenone with the U-Ni-B and U-Ni-A obtained from precipitated nickel, which was prepared from nickel chloride solution with zinc dust by the ordinary methods[2,3], dried at about 100°C, and left standing for a week in the air. The results are shown in Table II. These results do not differ from those obtained with the normally prepared U-Ni-B and U-Ni-A. Therefore, contact with air is safely permitted for precipitated nickel. It may not be necessary for the water for washing to be distilled in the preparation of precipitated nickel.

One of the features of the Urushibara nickel catalyst is that it is not self-inflammable by contact with air under ordinary conditions. Consequently, nickel can be recovered from such waste catalyst as nickel chloride which can be used again for the preparation of the Urushibara nickel catalyst. But the operation may be troublesome and expensive. If recovered Urushibara nickel can be repeatedly used in place of the precipitated nickel, the time for preparing the precipitated nickel and the cost of nickel chloride will be saved. For the purpose of attaining this request a series of experiments was carried out to regenerate the active catalyst directly from recovered catalyst (Table III).

First, the U-Ni-B was prepared from the mixture of recovered U-Ni-A and zinc dust by treatment with sodium hydroxide solution. The regenerated catalyst was found to be useful enough for the reduction of acetophenone though it was somewhat less active (Exp. No. 31). The cause of this reactivation was considered to result from the removal of adsorbed substances on the surfaces of nickel particles by hydrogen gas generated from zinc dust with caustic alkali. Then the catalyst prepared from recovered U-Ni-A and zinc dust by treatment with acetic acid was also expected to have considerable activity. In fact, such a catalyst proved to be highly active and gave a better result than that obtained with the original U-Ni-A (Exp. No. 32). To save the amount of zinc dust, the next catalysts were prepared by using one half or one fourth the amount of zinc dust as the quantity used for preparing the catalyst in Exp. No. 32. They had also high activities (Exp. Nos. 33 and 34), and gave practically the same results as those obtained with the normally prepared U-Ni-A (cf. Exp. Nos. 112—115 in Table I). If the existence of a small amount of zinc is enough to reactivate the recovered catalyst, the recovered U-Ni-B and U-Ni-CB may become active by being treated with acetic acid. Actually, each of the catalysts prepared from the recovered U-Ni-B and U-Ni-CB used in Exp. Nos. 11 and 19, gave a better result than those obtained with the original catalysts (Exp. Nos. 35 and 36). As the recovered U-Ni-B and U-Ni-CB contain only a small quantity of zinc, only a little hydrogen gas is evolved by the digestion with acetic acid. Accordingly, zinc dust is supposed to be excluded from the reagents necessary for the renewal of the catalyst. Thus some catalysts were prepared from recovered U-Ni-A by being treated with acetic acid only, and these catalysts were also found to be highly active (Exp. Nos. 37, 38 and 39). In these cases, however, nickel itself reacted vigorously with hot acetic acid, and solid, adsorbing hydrogen gas, came up to the surface of the green solution. In consideration of the results described above, acetic acid must have, in case of preparing the U-Ni-A, some activating effect on the surfaces of nickel particles besides the chemical function of generating hydrogen gas and removing deactivating substances (basic zinc chloride and others). Probably one important function of acetic acid may consist in eroding the surfaces of nickel particles and creating new ones. This assumption accounts for the reactivation of recovered catalysts and also for the fact that the U-Ni-A has not high activity, when the digestion with acetic acid is interrupted before the solution turns green by the formation of nickel ion[1]. The discussion as to whether or not the precipitated nickel has inherently active nickel surfaces seems not to be important.

Summary

Catalytic reduction of acetophenone with various Urushibara nickel catalysts was studied under high pressure. The U-Ni-A with a small amount of alkali was found to be the most useful. The U-Ni-CB and U-Ni-CA were also highly active as they were in case of the reduction of benzophenone. The activity of the U-Ni-A and U-Ni-B, prepared from preserved precipitated nickel, was the same as that of the catalysts obtained from the freshly prepared precipitated nickel. In addition, it was found that the recovered Urushibara nickel catalyst could be repeatedly used after a simple regeneration process especially in the form of U-Ni-A. Such a regenerated catalyst had practically the same activity as that of the normally prepared U-Ni-A.

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