High Pressure Reduction of Organic Compounds with Urushibara Catalyst. VI(1). A New Type of Urushibara Nickel Catalyst

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In 1952 Urushibara and Chuman discovered a new catalyst, which was prepared from precipitated nickel. Aqueous nickel chloride solution was treated with zinc dust, and the precipitated nickel was digested with caustic alkali to obtain the active catalyst for hydrogenation(2). The procedure for the preparation of this catalyst has been successively modified to obtain the more active catalyst. It was also found that a highly active catalyst can be obtained by digesting the precipitated nickel with either aqueous caustic alkali or aqueous acetic acid, and the former was named Urushibara nickel B or U-Ni-B in abbreviation(3), and the latter Urushibara nickel A or U-Ni-A in abbreviation(4). Recently it was proved that the activity of the U-Ni-B is comparable with that of Raney nickel catalyst for hydrogenation under ordinary pressure(5).

An application of Urushibara nickel catalyst to the hydrogenation of various organic compunds under high pressure

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1) Part V: K. Hata, S. Taira and I. Motoyama, This Bulletin, **31**, 776 (1958).

2) Y. Urushibara, ibid., **25**, 280 (1952).

3) Y. Urushibara and S. Nishimura, ibid., **27**, 480 (1954).

4) Y. Urushibara, S. Nishimura and H. Uehara, ibid., **28**, 446 (1955).

5) S. Nishimura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1741 (1957).

has been investigated since 1954. During the successive investigations it was noticed that this catalyst could not hydrogenate aromatic compounds such as benzene, aniline, etc., even under severe conditions, although it was very effective for the hydrogenation of ethylenic compounds, aldehydes, ketones, nitro compounds, oximes, nitriles and simple phenols[6-9]. To get rid of this defect, an attempt was made to prepare a new type of Urushibara catalyst from nickel chloride and aluminum instead of zinc. Some information on the new Urushibara catalyst thus obtained, named Urushibara nickel BA or U-Ni-BA in abbreviation, was reported briefly in the preceding paper[1].

In the present paper, the hydrogenation of several aromatic compounds with this new catalyst and certain useful modifications of procedure for the preparation of this new catalyst are described.

Hydrogenation of Aromatic Compounds

The Urushibara nickel BA was found to be effective for the hydrogenation of aromatic nucleus which had not been hydrogenated with U-Ni-B or U-Ni-A. The results of the hydrogenation of some aromatic compounds are summarized in Table I. The hydrogenation of phenol can also be attained with either U-Ni-B or U-Ni-A, but it takes much time to complete the reaction with these catalysts even under considerable high temperature. With U-Ni-BA, however, phenol can be easily hydrogenated at lower temperature. It is evident from these results that the U-Ni-BA has a high activity for the hydrogenation of aromatic nucleus, and that the use of aluminum grains instead of zinc dust brings about a favorable change on the property of Urushibara catalyst. It is obvious that the difference between the properties of these two kinds of Urushibara catalysts is due to the difference of the metal combined with nickel in each catalyst.

Preservability of Urushibara Catalyst

Preparation of catalyst has been generally thought to be troublesome and difficult, but it is not true for the preparation of Urushibara nickel catalyst, because it is prepared by simple operations in only an hour or less. However, the preparation of U-Ni-BA from nickel chloride and aluminum grains requires somewhat longer time than that of the other Urushibara catalysts from nickel chloride and zinc dust. A certain useful modification has been made in the procedure for the

TABLE I. HYDROGENATION OF ORGANIC COMPOUNDS

Catalyst: U-Ni-BA containing about 2 g. of nickel,
Sample: 10 g., Solvent: 99% ethanol 50 cc.

Sample	mol.	Initial pressure atm.	Temp. °C	Time hr.	Hydrogen absorbed mol.	Products & Yield* %
Phenol	0.106	66	70∼110	1.0	0.355	Cyclohexanol (79)
Methyl salicylate	0.066	65	84∼115	2.0	0.190	Ethyl hexahydrosalicylate** (65)
Ethyl benzoate	0.066	54	106∼150	2.5	0.231	Ethyl hexahydrobenzoate (82)
Diethyl phthalate	0.045	68	114∼154	3.0	0.145	Diethyl hexahydrophthalate (91)
Benzene	0.128	100	100∼142	3.0	0.403	Cyclohexane (70)
Ethylbenzene	0.094	70	100∼143	4.0	0.308	Ethylcyclohexane (63)
Aniline	0.108	96	150∼209	3.5	0.334	*N*-Ethylcyclohexylamine*** (71) Dicyclohexylamine
Acetanilide	0.074	75	120∼206	5.0	0.236	Hexahydroacetanilide (77)

* Increased yields may be obtained in case of large scale operations.

** Ester exchange was observed during hydrogenation, and yet the product was found to contain an appreciable amount of methyl ester.

*** *N*-Ethylation was observed during hydrogenation (cf. H. I. Cramer et al., Ref. 10)

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6) K. Hata et al., ibid., **77**, 1405 (1956).

7) K. Hata, S. Taira and T. Higase, ibid., **78**, 186 (1957).

8) I. Motoyama, ibid., **79**, 1296 (1958).

9) K. Hata, S. Taira and Y. Satomi, ibid., **79**, 1298 (1958).

10) H. I. Cramer and H. Adkins, *J. Am. Chem. Soc.*, **52**, 4354 (1930).

TABLE II. HYDROGENATION OF PHENOL TO CYCLOHEXANOL
Catalyst: U-Ni-BA (2 g. Ni), Sample: phenol 10 g.,
Solvent: ethanol 50 cc. A small amount of NaOH was added.

Solvent for preservation	Period of preservation day	Initial pressure atm.	Temp. °C	Time hr.	Hydrogen absorbed l. at 20 °C, 1 atm.	Isolated cyclohexanol g.
(Not preserved)	0	66	70～110	1.0	8.6	7.9
Water	6	50	76～117	1.5	7.8	8.5
〃	90	75	79～120	1.5	8.0	8.2
Ethanol	6	50	68～119	1.5	7.6	8.3
〃	90	77	74～120	1.7	7.9	7.9
None (dry)	1	65	66～112	1.5	7.5	7.7
〃	15	82	70～120	1.3	7.9	6.3
					(calcd. 7.7	10.6)

TABLE III. HYDROGENATION OF ORGANIC COMPOUNDS
Catalyst: U-Ni-BA (2 g. Ni) prepared from the precipitated nickel preserved in dry state.

Sample	mol.	Solvent	Initial pressure atm.	Temp. °C	Time hr.	Products & Yield %
Benzene	0.27	None	80	90～150	2.5	Cyclohexane (77)
Aniline	0.11	Ethanol	75	150～208	3.0	*N*-Ethylcyclohexylamine (69) Dicyclohexylamine
Aniline	0.11	Cyclohexane	70	150～215	3.0	Cyclohexylamine (35) Dicyclohexylamine (38)
Pyridine	0.10	Cyclohexane	65	150～218	3.0	Piperidine (86)

preparation of U-Ni-BA catalyst, so as to shorten the time required for the preparation. The principle of the modification is to prepare the U-Ni-BA catalyst from preserved nickel precipitate, which is previously made in large quantities. After the ion-exchange reaction between nickel chloride and aluminum grains, the precipitated nickel is preseved in a proper manner, and then treated with aqueous alkali to make up the U-Ni-BA catalyst when it is used for hydrogenation. Such preservation of the precipitate, however, was expected to cause deactivation of the catalyst, because it is presumed that active nickel surface are inherently present in the precipitate but are covered with certain water-insoluble substances, and consequently the precipitated nickel itself, as it is precipitated, is ineffective as catalyst, unless it is treated with alkali or acid[4].

The activity of the catalyst prepared from the preserved precipitate was examined by the hydrogenation of phenol. The precipitate was preserved from a day to three months in the following three ways: in distilled water, in 99% ethanol and in dry state. Each preserved precipitate was then treated with 20% aqueous sodium hydroxide solution to prepare the catalyst. The results of the hydrogenation of phenol are summarized in Table II. As shown in Table II, each 3 mol. of hydrogen were absorbed with the catalyst prepared from the preserved precipitate as well as with that immediately treated with alkali after the ion-exchange reaction, although the time required for hydrogenation was somewhat longer with the former catalyst. About 8 g. of cyclohexanol were isolated similarly from every reaction mixture. Thus, contrary to expectation, no remarkable deactivation was found with U-Ni-BA catalyst by any preservation of the precipitated nickel. The precipitate preserved in dry state is more convenient for use than those preserved in water or ethanol.

When the dried precipitate is exposed to air under ordinary pressure, it is rapidly oxidized generating a considerable amount of heat. Therefore, it is desirable to keep it under reduced pressure, especially in case of a large scale operation.

Additional results of the hydrogenation with the catalyst prepared in this way are summarized in Table III. It can be seen from these results that this catalyst still maintains the similar catalytic activity as the catalyst prepared from precipitated

TABLE IV. PHYSICAL CONSTANTS OF THE PRODUCTS

Compound	b. p. °C/mmHg.	Refractive index (°C)	Derivative (m.p., °C)
Cyclohexanol	157~162		3,5-Dinitrobenzoate (112)
Ethyl hexahydrosalicylate	115~119/19	1.4674(16.0)	
Ethyl hexahydrobenzoate	87~88/20~21	1.4437(22.0)	Amide (183~187)
Diethyl hexahydrophthalate	145.5/20	1.4523(22.0)	Free acid (197~198)
Cyclohexane	78~ 80	1.4315(23.0)	
Ethylcyclohexane	125~132	1.4315(27.5)	
N-Ethylcyclohexylamine	160~167		Hydrochloride (183~185)
Cyclohexylamine	130~136	1.4673(13.5)	*N*-Acetyl (104~105)
Dicyclohexylamine			Hydrochloride (above 210) (Found: N, 6.56%)
Hexahydroacetanilide	103~104 (m. p.)		
Piperidine			*N*-Benzenesulfonyl (93.5)

nickel immediately after the ion-exchange reaction (cf. Table I).

It is quite interesting that the U-Ni-BA catalyst prepared from the precipitated nickel being kept in air for a long time maintains its high catalytic activity for the hydrogenation of aromatic compounds.

The modification in this way can be applied not only to the new Urushibara catalyst but also to the old ones.

Experimental

Apparatus.—Hydrogenation was carried out in an autoclave of stainless steel with a magnetic stirrer (capacity: 200 cc., rate of stirring: about 60 strokes per min.).

Catalyst.—Catalyst was prepared according to the procedure previously reported[1] and washed thrice with 99% ethanol, when the hydrogenation was carried out in ethanol. When another solvent was employed, the catalyst was washed first thrice with 99% ethanol and then thrice with the solvent.

Preservation in Dry State. — The precipitate, obtained from 100 ml. of aqueous nickel chloride solution containing 40 g. of $NiCl_2 \cdot 6H_2O$ and 50 g. of aluminum grains (40~80 meshes), was washed well with distilled water, then collected on Büchner funnel and dried under reduced pressure. Final weight of the precipitate was about 70 g.* in all. Each 14 g. of the dry precipitate, which contains 2 g. of nickel, was treated with 250 g. of 20% aqueous sodium hydroxide solution before the application for hydrogenation.

Materials.—All substances used for hydrogenation were purified by redistillation or recrystallization except those with special indication.

Methyl salicylate, ethyl benzoate and diethyl phthalate were respectively prepared by usual esterification[11] from corresponding acids.

Benzene was purified by treatment first twice with anhydrous aluminum chloride[12], then with a large amount of U-Ni-A[13]. The purified benzene was redistilled before hydrogenation.

Products.—Reduction products were fractionally distilled except those with special indication, and were identified through appropriate derivatives. When the products were liquid, their refractive indices were measured. Physical constants of the products are summarized in Table IV.

Cyclohexane and ethylcyclohexane were respectively separated from the solvent by adding a large quantity of water to the reaction mixture, dried over anhydrous calcium chloride and distilled.

Piperidine was converted to its hydrochloride by adding an excess of concentrated hydrochloric acid to the reaction mixture after removal of catalyst. The solvent was distilled off and the residue was completely dried up under reduced pressure. Then, the resulting piperidine hydrochloride was purified by recrystallization from 99% ethanol.

Summary

A new Urushibara nickel catalyst, U-Ni-BA, was prepared from nickel chloride and aluminum grains. This new catalyst was found to be highly active for the hydrogenation of aromatic nucleus, contrary to the older Urushibara nickel catalyst, U-Ni-A or U-Ni-B.

The preservability of the catalyst was examined: the precipitate, obtained by the reaction of nickel chloride with aluminum grains (or zinc dust), was kept for a long time in solvent or in dry state, and a similarly active catalyst could be obtained by digesting the preserved precipitate with aqueous caustic alkali.

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* This weight varies with experimental condition.

[11] E. Fischer and A. Speier, *Ber.*, **28**, 3253 (1895).

[12] R. J. Graul and J. V. Karabinos, *Science*, **104**, 557 (1946).

[13] H. N. Holmes and N. Beeman, *Ind. Eng. Chem.*, **26**, 172 (1934).

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