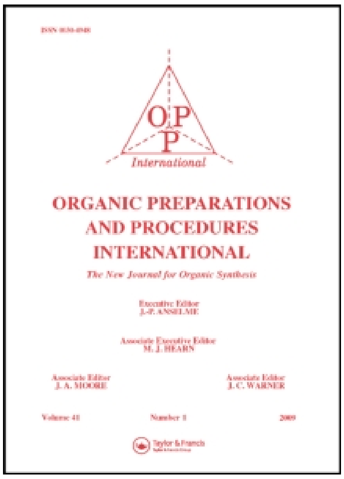

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THE URUSHIBARA HYDROGENATION CATALYSTS A REVIEW

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A REVIEW

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A REVIEW

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INTRODUCTION AND HISTORICAL BACKGROUND

The Urushibara catalysts have not received the widespread reputation and utilization that their versatility and ease of preparation should command. The present review gives a brief but nonetheless general survey of the preparation and the applications of the Urushibara catalysts. The reader is referred to the monograph[1] on this subject for a detailed discussion of many aspects which are either covered only cursorily or not at all in this review.

In 1951, Urushibara and his colleagues discovered a new type of hydrogenation catalysts prepared from precipitated metals. In contrast to previous catalysts which were discovered by chemists investigating catalytic reactions, the Urushibara catalysts (abbreviated U-catalysts) were not the result of research in an unknown field of catalytic chemistry or of a mere accident. About twenty years ago, Urushibara and his group undertook an investigation to find a new method for the reduction of estrone to estradiol at the request of a hormone manufacturing company. Indeed, in 1933, Schwenk of Schering A. G. had discovered a process suitable for industrial purposes and obtained a Japanese patent,[2] which covered almost all the methods of reduction known at that time. In another Japanese patent[3] issued to Schering A.G., the addition of Raney alloy to an alkaline aqueous solution of estrone efficiently combined the catalytically active Raney nickel with nascent hydrogen, both being generated by the action of aqueous alkali on the Raney alloy.

Then, Urushibara got the idea that some common metal powder might exhibit catalytic activity if it was combined with nascent hydrogen. This simple concept was translated into practical application by the preparation of a fine nickel powder precipitated from an aqueous solution of a nickel salt by another metal of greater ionization tendency such as zinc or aluminum. Although the results obtained in the early stages of experimentation were quite disappointing, continued intensive research came to fruition by the preparation of a new catalyst of high activity, comparable to that of Raney nickel. The catalysts thus obtained were named the Urushibara catalysts after name of the discoverer.

1. GENERAL FEATURES OF THE U-CATALYSTS

The Urushibara catalysts comprise various catalysts prepared by essentially similar processes. An extremely simple procedure for preparing the catalysts is as follows. The catalyst metal is precipitated in powder or fine granular form from an aqueous solution of its salt, with another metal of a greater ionization tendency. The precipitated metal is then digested with the appropriate base or acid. Catalytically active nickel, cobalt, iron, copper and iron containing a small portion of nickel or cobalt, are thus obtained.

A shorthand nomenclature has been devised for the Urushibara catalysts. The letter U (after the name of the discoverer) is followed by the catalyst metal symbol. The precipitating metal is zinc dust unless specified as described below. The letter C appearing sometimes after the catalyst metal symbol signifies that both the precipitation and the digestion processes were carried out at or below room temperature. Then follows the digesting medium, abbreviated A for acid (usually acetic acid or sometimes propionic acid) or B for alkali (almost invariably sodium hydroxide). The chemical formula of ammonia is substituted for B when it is used as the digesting medium; similarly, HCl is added in parentheses when hydrochloric acid is used as the digesting medium. The symbol A placed after that of the digesting medium, such as AA or BA, indicates that aluminum is used as the precipitating metal. For the Urushibara iron catalysts, Roman numerals II and III are placed in parenthesis after Fe to indicate from which iron salt the catalyst metal was precipitated; in the case of iron, the digesting medium is not specified unless different from acetic acid. In especially activated iron catalysts, the activating metal content and its symbol are placed in parentheses. An (s) placed last denotes that the metal was precipitated by the simplified method. The following examples will serve to illustrate those rules.

U-Ni-CA[4]: Catalyst metal is nickel, precipitated by zinc dust and digested with acetic acid; both processes were conducted at or below room temperature.

U-Ni-AA[5]: Catalyst metal is nickel, precipitated by aluminum grains and digested with (acetic) acid.

U-Co-A(s)(HCl)[6]: Catalyst metal is cobalt, precipitated by zinc dust via the simplified method and digested with hydrochloric acid.

U-Fe(III)-BA[7]: Catalyst metal is iron (from iron(III) salt), precipitated by aluminum grains and digested with sodium hydroxide.

U-Fe(II)[7]: Catalyst metal is iron (from iron(II) salt), precipitated by zinc dust and digested with (acetic) acid.

U-Fe(III)-Ni(Fe:1,Ni:0.01)[7]: Catalyst metal is iron (from iron(III) salt) containing 1% of nickel, precipitated by zinc dust.

The salts most often used are the chlorides and sometimes the acetates. The precipitating metal is usually zinc dust or granular aluminum. The digesting reagent may be chosen from among the following: caustic alkali, ammonia, acetic acid, propionic acid and hydrochloric acid. However, sodium hydroxide or acetic acid is generally used. The digestion process (with the basic or acidic reagents), removes basic salts of the precipitating metals covering the surface of the catalyst to expose the active surface. The reduction of various organic compounds with Urushibara nickel gives results which are very similar to those obtained with Raney nickel.

The activation of precipitated nickel by a caustic alkali remained unexplained for a long time, until it was discovered that precipitated nickel, even if it was well washed with water to remove soluble chloride ions completely, released chloride ions on digestion with caustic alkali. It was suggested that a chloride, which was insoluble in water but soluble in aqueous alkali, was adhering to the precipitated nickel and X-ray diffraction studies showed this to be zinc hydroxide chloride.[8]

Commercial aluminum powder is too finely pulverized to allow a moderate exchange reaction to take place since the extremely violent reaction rendered the preparation very difficult. Hence a procedure was devised in which aluminum grains of moderate size were employed to produce precipitated nickel under special conditions. The precipitated nickel, subjected to treatment with caustic alkali solution, reacted as expected and gave rise to a new type of U-catalyst, U-Ni-BA.[9] U-Ni-BA works well in the hydrogenation of benzene to cyclohexane, which cannot be realized by ordinary U-Ni-A or U-Ni-B prepared with zinc dust as the precipitating metal. Although precipitated metals without digestion by alkali or acid do not catalyze hydrogenation with hydrogen gas under ordinary conditions, we recently found that various organic compounds can be reduced when they were refluxed with water in the presence of precipitated nickel.[10] An unique feature of the reductions with precipitated nickel is the use of water as a hydrogen donor, thus making the use of any acid or alkali generally unnecessary.

The Urushibara catalysts can be used for hydrogenation or reductions under a variety of reaction conditions, including ordinary or high pressures at room or elevated temperatures, and in either the liquid or the vapor phase. The most suitable modification of the catalyst is chosen for the purpose at hand. The usage has been further extended to other reactions, for instance, desulfurization, dehydrogenation, and hydration.

The general characteristics common to various Urushibara catalysts may be summarized as follows:

(1) The preparation of U-catalysts is rapid and very simple. They can be prepared from commercial materials by simple procedures in an hour or less. Their activities are nevertheless quite high.

(2) The quality of the materials is not critical. In general, "chemically pure" grade reagents serve the purpose. Tap water may be used except for the last washing of the finished catalyst, though the use of distilled water is preferable throughout the whole procedure.

(3) The dried precipitated metals, which are the precursors of U-catalysts, can be stored for a long time without detriment to the activity of the catalysts.

(4) The handling of U-catalysts is safe and easy, as they are not flammable upon short contact with air,* in contrast to Raney catalysts which are pyrophoric.

(5) Used catalysts can easily be recovered and regenerated without any noticeable decrease of their activity.

(6) They may be used for multifarious purposes such as hydrogenation under various conditions, dehydrogenation, reductive desulfurization, and so on. The applications and the activities of U-catalysts are comparable to Raney catalysts.

(7) Under selected conditions, U-catalysts can be used for special purposes such as partial and selective hydrogenation, vapor-phase hydrogenation, etc.

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*Isolated cases of ignition are probably the result of unnecessarily long contact with air.

2. PREPARATION OF SELECTED URUSHIBARA CATALYSTS

The preparation of Urushibara catalysts is carried out in two stages. The first stage involves the deposition of metal by reaction between a soluble salt of the catalyst metal and a metal which is more electropositive. The second stage consists in the treatment of the precipitated metal with alkali or acid to yield an active catalyst. It has been established that the reaction conditions in the first stage have a critical influence upon the activity of the catalyst which is produced.

Zinc, aluminum, and magnesium have been tested for use as the precipitating metal. Zinc dust has been used exclusively in the preparation of ordinary Urushibara catalysts, owing to its ease of handling.

Although no extensive experimentation has been carried out in this respect, the size of the preparations of the catalysts herein described may be scaled up to about ten times the quantities given.

2.1. Standard Preparation of U-Ni-B[11] and U-Ni-A[12]

2.1a. Precipitated Nickel (Ppt-Ni)

Ten grams of zinc dust are placed in a 100 ml round-bottomed flask and 3 ml of distilled water are added. Contamination of the zinc dust with zinc oxide or hydroxide is not harmful. An efficient mechanical stirrer nearly reaching the bottom of the flask is installed and the flask is heated on a boiling water-bath. Then a hot (heated to boiling) solution of 4 g of nickel chloride ($NiCl_2 \cdot 6H_2O$) in 10 ml of distilled water is added cautiously but rapidly (within a few seconds [Note 1]) to the vigorously stirred mixture of zinc dust and water. During the addition of the hot solution, stirring must not be allowed to stop. When the vigorous reaction subsides, the solid is collected on a sintered glass funnel by suction and washed with about 200 ml of hot water. The solid mass is transferred into a 300 ml beaker or Erlenmeyer flask for digestion. Decantation with several portions of hot water in a beaker may be substituted for the washing process.

NOTE 1. Since the discharge time of an ordinary pipet is too slow for the addition of the nickel chloride solution to the zinc dust (which inevitably causes a reduction in catalytic activity), a pipet whose tip has been cut off allowing the solution to run out quickly and uniformly, should be used. The apparatus shown in Fig. 1, equipped with an inlet tube through which the nickel chloride solution can be poured from a beaker, allows the uniform addition of solution in 2 to 3 seconds.

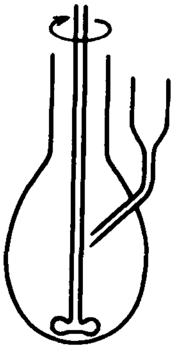

Fig. 1. Flask for the Preparation of the Precipitated Metal

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2.1b. Preparation of U-Ni-B[11]

The precipitated nickel containing excess zinc and accompanying insoluble zinc compounds is activated to U-Ni-B in the following way; to a 300 ml beaker or Erlenmeyer flask containing 160 ml of 10% sodium hydroxide solution [Note 1] is added the Ppt-Ni obtained above [Note 2]. It is recommended that a part of the sodium hydroxide solution be used to wash out the Ppt-Ni from a sintered glass funnel. Since the Ppt-Ni reacts with the sodium hydroxide solution with vigorous evolution of hydrogen, care should be taken that the contents do not boil over. The reaction vessel is then heated on a water bath at 50-55° with slow mechanical stirring for 15-20 min [Note 3]. The supernatant liquid is decanted, and the remainder washed with two or three 40 ml portions of distilled water, which has been boiled in advance and cooled to 50-60°. Each time the wash-water is decanted, and the catalyst is washed with the solvent, e.g., ethanol, to be used in the subsequent reduction, and then transferred together with the solvent to the reduction vessel. The solid should always be covered with water or solvent after the alkali treatment, so that contact with air is minimized [Note 4].

The product is U-Ni-B, a dark gray powder-like solid. U-Ni-B, prepared from nickel chloride containing 1 g of nickel, consists of about 0.95 g of nickel and 4-5 g of zinc, together with small amounts of zinc oxide and zinc hydroxide, amounting to 5-7 g in weight.

NOTE 1. The use of 80 ml of 10% sodium hydroxide solution instead of 160 ml yields a more active catalyst; however, it is more bulky and the gross weight amounts to as much as 10 g, because the zinc is dissolved to a lesser extent.

NOTE 2. This procedure was designed so as to minimize contact with air. However, it has been verified that drying of the precipitated nickel has little effect upon catalytic activity and one may take an alternative procedure, in which the precipitated nickel is first placed in a beaker, and sodium hydroxide solution is added to it with stirring. The latter process is preferred because liquid overflow due to the vigorous reaction can easily be controlled.

NOTE 3. The activity of the catalyst is reduced when the temperature at which the precipitated nickel is digested with sodium hydroxide solution is too high, or when digestion continues too long that the evolution of hydrogen gas subsides.

NOTE 4. This is the recommended procedure for obtaining catalysts of high activity although short contact with air is not particularly harmful.

2.1c. Preparation of U-Ni-A[12]

The catalyst is prepared by digesting the precipitated nickel with 160 ml of 13% acetic acid [Note 1], using the same procedure as in the alkali digestion except that the mixture is first stirred for 4-6 minutes at room temperature (or at 40° for about 4 min). The evolution of hydrogen gas gradually subsides and most of the zinc and zinc compounds dissolve, a black powder-like solid having adsorbed hydrogen floats on the surface of the solution. When the solution becomes greenish [Note 2], it is cautiously filtered and the black solid is collected on a sintered glass funnel (with the same caution so as to minimize contact with air). It is washed with 200 ml of distilled water, which has been boiled in advance and cooled to 50-60°, then finally with the solvent to be used in the subsequent reduction. U-Ni-A obtained in this way contains 0.80-0.85 g of nickel and a small amount of zinc, weighing 1.3-1.4 g in total.

U-Ni-A is more conveniently used than U-Ni-B, a small amount of sodium hydroxide being added for the reduction of carbonyl compounds and nitriles.

NOTE 1. Catalyst of somewhat higher activity is obtained when 160 ml of 20% propionic acid is used instead of acetic acid and digestion is continued for 4-5 min at 50°.

NOTE 2. Part of the nickel dissolves in acetic acid and produces a green color. When the solution is colorless, stirring should be continued until the color develops. In order to obtain a catalyst of high activity, it is necessary to allow digestion to proceed until green coloring develops. However, the catalyst should be filtered as soon as the color appears, because a longer digestion diminishes the nickel content.

2.2. Preparation of U-Ni-NH_3[13]

Precipitated nickel (containing about 1 g of nickel) prepared as in 2.1a, is added to 100 ml of 14% aqueous ammonia and the mixture is stirred gently on a water bath at 50-60°. After 15-20 min digestion, the evolution of hydrogen gradually ceases. The mixture is left to stand for a while, and the supernatant liquid is decanted. The solid is then washed twice by decantation, using 20 ml of methanol or ethanol for each wash. U-Ni-NH_3 thus obtained, is a grayish black powder and weighs about 8.6 g.

It exhibits an activity comparable to that of Raney nickel in the pressure hydrogenation of adiponitrile to 1,6-hexamethylenediamine.

2.3. U-Ni Catalysts Prepared from Nickel Acetate[4]

Nickel acetate, in place of nickel chloride, gives an Urushibara nickel catalyst of similar activity. As the reaction between nickel acetate and zinc dust is more violent and accompanied by strong bubbling of the reaction mixture, it must be carried out in a larger vessel with strong stirring.

The difficulty in separating the precipitated nickel prepared from nickel acetate has led to the discovery of a convenient "one pot" preparation of active U-Ni-A and U-Ni-B (however, the "one pot" operation is not recommended from nickel chloride). These preparations are described below.

Preparation of U-Ni-B from Nickel Acetate. A hot solution of 4.24 g of nickel acetate tetrahydrate in 20 ml of water is added with stirring to a mixture of 10 g of zinc dust and 10 ml of water contained in a 500 ml beaker on a boiling water bath. As the vigorous reaction takes place and the mixture begins to inflate, strong agitation is required to prevent the contents from spilling over.

When the reaction subsides, 200 g of 10% sodium hydroxide solution is cautiously added with stirring. The temperature of the mixture is kept at 50-55° for 15 min with occasional stirring. When the solid matter settles, the supernatant liquor is decanted and the solid is washed with two 100 ml portions of hot water, then with two 50 ml portions of the solvent to be used in the reduction, e.g., ethanol. In this way a bulky catalyst, weighing as much as 8.5-10.5 g, is obtained. The catalyst contains about 1 g of nickel, together with considerable amounts of zinc and zinc oxide and a very small amount of alkali.

Preparation of U-Ni-A from Nickel Acetate. The precipitated nickel is prepared as described above. Then 160 ml of 13% acetic acid is added and the mixture is left standing with occasional stirring until the evolution of hydrogen ceases and a solid rises to the surface of the greenish solution. The solid is collected on a sintered glass filter and washed with 200 ml of hot water, then with 100 ml of ethanol. The catalyst contains only small quantities of zinc and zinc oxide and weighs about 0.7 g.

Regarding the reduction of benzophenone, it has been established that U-Ni-B prepared from nickel acetate is somewhat more active than that from nickel chloride, whereas the reverse is true with U-Ni-A.

2.4. Preparation of U-Ni-C Catalysts[4]

In order to obtain a precipitated metal of small particle size, it is necessary to retard the rate of the exchange reaction, which depends on several factors: the difference in the standard electrode potentials of zinc and the catalyst metal, the fineness of the zinc dust, the concentration of the solution of metal chloride, the temperature at which the precipitated metal is prepared, and the efficiency of agitation. Of these, only the temperature can be easily controlled; the other factors are mainly decided by the nature or quality of chemicals. At low temperatures, the exchange reaction takes place slowly and the metal separates out uniformly on the surface of the zinc dust, thereby giving a catalyst of small particle size. The precipitated nickel prepared at low temperatures gives highly active Urushibara nickel catalysts, U-Ni-CA and U-Ni-CB. Their preparation, however, requires so much time that speed of preparation, one unique characteristic of the Urushibara catalysts, is lost.

Preparation of U-Ni-CB and of U-Ni-CA

To a 100 ml flask containing 10 g of zinc dust and 4 ml of water is added 10 ml of an aqueous solution containing 4.04 g of nickel chloride, $NiCl_2 \cdot 6H_2O$. The mixture is stirred at room temperature, or while being cooled with water or ice, until the green color of the nickel ion disappears. Stirring may be interrupted after the first hour, as the ion-exchange reaction is practically complete after this period. The mixture should be left standing thereafter until the remaining faint color disappears. The whole process requires 3-4 hours. In the preparation of precipitated nickel on a large scale, it is advisable to cool the mixture with ice during the ion-exchange process. The slushy precipitate is transferred to a 300 ml beaker and washed with 200 ml of cold water. To digest the precipitated nickel, 160 g of cold 10% sodium hydroxide solution is added to the beaker and the mixture is stirred for an hour. Cooling with water or ice is often required. When most of the solid settles, the upper liquor is carefully decanted and the solid is washed with two 100 ml portions of cold water and then with two 50 ml portions of solvent. The catalyst contains about 1 g of nickel containing zinc, zinc oxide, and a trace amount of alkali, weighs 8-11 g.

Only the digestion process is different for U-Ni-CA. The precipitated nickel prepared as above is transferred to a 500 ml beaker and is carefully treated with 200 ml of 10% acetic acid while being cooled with water. After about 5 min, the liberation of hydrogen subsides and a solid comes to the surface of the green solution. The solid is collected on a sintered glass filter and washed with 200 ml of cold water, and then with 100 ml of solvent. The catalyst is a fine powder and weighs 0.6 to 0.8 g. It contains 0.4-0.5 g of nickel together with small amounts of zinc and zinc oxide.

2.5. Simplified Methods for the Preparation of Urushibara Catalysts[6]

2.5a. Precipitated Nickel (Ppt-Ni)

Commercial nickel chloride crystals ($NiCl_2 \cdot 6H_2O$), 4.04 g, are added all at once to a 50 ml beaker containing 10 g of zinc dust well mixed with 4 ml of water. The mixture is stirred with a glass rod and the reaction begins and abruptly becomes very vigorous; after a few minutes, the mixture inflates into a slushy mass. It is then washed with 200 ml of cold water, and the wash-water is removed by filtration or decantation. The precipitated nickel weighs about 13.5 g and contains about 1 g of nickel, together with zinc, zinc oxide, and zinc hydroxide chloride.

2.5b. U-Ni-B(s) and U-Ni-A(s)

The digestion process is the same as that described for U-Ni-B and U-Ni-A except that in the latter case 20% acetic acid is used instead.

2.6. Preparation of U-Ni-BA and U-Ni-AA

The nickel is precipitated from its chloride solution with aluminum grains (40-80 mesh) instead of zinc dust. The reaction must be conducted below 70°.

U-Ni-BA,[9] prepared by digestion with 20% sodium hydroxide solution is a black powder, consisting of nickel and small amounts of aluminum and alkali; it shows a specific activity for hydrogenation of aromatic rings.

U-Ni-AA,[5] prepared by digestion with 40% acetic acid, saturated with sodium chloride (about 89 g of sodium chloride are required to saturate 385 ml of 40% acetic acid), is particularly appropriate for vapor-phase hydrogenation.

For the quantities of nickel chloride using the previous preparations, 10 g of commercial aluminum grains of the specified mesh size are cleansed first with either 3% sodium hydroxide or 6N hydrochloric acid (CAUTION: vigorous reaction). Great care should be exercised in controlling both the precipitation and the digestion processes. The digestion process for U-Ni-BA requires more time than for U-Ni-B.

2.7. Preparation of Urushibara Cobalt, Copper and Iron Catalysts

The preparation of the Urushibara cobalt (U-Co), copper (U-Cu) and iron (U-Fe)[7] catalysts follows along essentially the same lines as that described for nickel; Reference 1 may be consulted for specific details.

As cobalt and nickel have almost the same atomic weights, the procedure for nickel can be used for cobalt without alterations. Precipitated copper hardly reacts with sodium hydroxide solution, thus rendering U-Cu-B practically useless. In the preparation of precipitated iron, it is best to utilize the simplified method. Both Fe(II) and Fe(III) chlorides can be used; the latter is preferred as no external heating is necessary in the precipitation step. Trace amounts of nickel or cobalt in the iron catalysts have been found to be beneficial in promoting hydrogenation. It is noteworthy that U-Fe is particularly effective in the partial hydrogenation of acetylenic compounds to *cis*-olefins, whereas U-Co is useful for the reduction of nitriles.

3. APPLICATIONS OF THE U-CATALYSTS

Generally, Urushibara catalysts are very similar to Raney catalysts in their catalytic action although much simpler to prepare and safer to use. They are utilized mostly in hydrogenation and reduction, but can also be used in dehydrogenation and reductive desulfurization, and sometimes in reductive alkylation, reductive condensation, hydration, etc.

Urushibara catalysts are usually employed in liquid-phase hydrogenation under either ordinary or high pressures, but can also be used in the vapor phase. Vapor-phase hydrogenations are best accomplished with U-Ni-AA, which allows the use of ordinary Sabatier apparatus.[5] Catalysts such as U-Ni-A require a special apparatus[14] such as illustrated in Fig. 2. U-Ni-A or U-Ni-B is most conveniently used for the usual hydrogenation.

The apparatus consists of a U-tube, 3 cm in diameter and about 50 cm long, made of hard glass (1.5-2.0 mm thickness). About 3/4 of the tube is filled with granulated pumice which has been purified beforehand by heating with conc. hydrochloric acid to dissolve any soluble matter. One end of the tube is filled with glass wool to support the pumice grains.

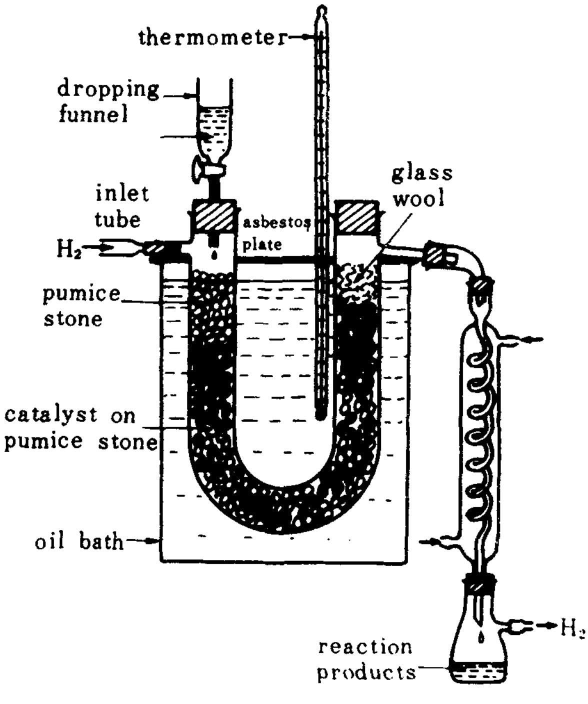

Fig. 2. Apparatus for Vapor-Phase Hydrogenation

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Freshly prepared U-Ni-A is washed well with water and then with ethanol to replace the water. Most of the ethanol is decanted, and the catalyst, suspended in the remaining ethanol, is poured together with the solvent onto the pumice stone in the U-tube. The catalyst settles on the pumice stone as it flows through the tube. The tube is tilted towards the glass wool-filled end to allow the catalyst to penetrate to the lower end and to spread over the whole surface of the grains of pumice. The tube is then filled with a supplemental amount of new pumice stone, and the remaining ethanol is decanted. The end of the U-tube which has no glass wool is fitted with a small dropping funnel, from which the sample liquid is to be added onto the pumice stone. A side tube underneath serves as the hydrogen inlet.

The other end of the U-tube is stoppered, and the side tube is fitted with a condenser which connects with a receiver for collecting the product. The end of the apparatus may also be connected to a receiver containing some absorbing agent, or to a Dry Ice trap when it is required to collect gaseous products. The U-tube is placed in an oil bath.

The procedure of reduction with this apparatus is as follows: the oil bath is heated to the boiling point of ethanol and hydrogen is passed through to remove the solvent in the form of vapor. After removal of the solvent, the temperature is raised. When the proper temperature is reached, the liquid sample is added dropwise from the dropping funnel into the tube. The liquid is vaporized on the hot pumice stone and is allowed to pass together with hydrogen gas onto the catalyst surface, where it is hydrogenated. The product is then carried to the condenser by the hydrogen, cooled to a liquid, and collected in the receiver. To carry out hydrogenation effectively, the addition of the sample should be as slow as possible, so that it can be mixed with a sufficient amount of hydrogen. The flow of hydrogen is continued for an additional 30-60 min at the specified temperature to complete hydrogenation and at the same time, to expel the product.

Although specific directions may be obtained from the references quoted in this review and in the monograph previously cited,[1] in general, for each 0.1-0.2 mole of substrate, the catalyst should contain approximately 1.0-1.5 g of the catalyst metal. Quite obviously, this ratio may be varied depending on the difficulty of the hydrogenation and the desired rate as well as on the temperature and the pressure at which the hydrogenation is to be conducted.

3.1. Hydrogenation

3.1a. Alkenes and Alkynes

Alkenes and alkynes are easily reduced to the corresponding saturated compounds in the liquid phase at either ordinary or high pressures. Vapor phase hydrogenation is equally suitable, particularly with U-Ni-AA which is the preferred catalyst. Selected examples are given in Table I. Apparently, the carboxylic acid group acts as a poison for the catalyst as is shown by the fact that whereas cinnamic acid is reduced with great difficulty, its sodium salt or even better, its ester absorbs hydrogen very rapidly.

3.1b. Aromatic Compounds

Ring hydrogenation proceeds only at high temperature and under pressure. U-Ni-BA appears to be the most widely useful catalyst (Table II).

TABLE I. Reduction of Alkenes and Alkynes

Compound	Catalyst	Temp.[a] (°C)	Pressure[b] (kg/cm^2)	Product	Yield (%)	Ref.
Na cinnamate	U-Ni-B	25	atm.	Na dihydrocinnamate	[c]	15
Ethyl cinnamate	U-Ni-B	25	atm.	ethyl dihydrocinnimate	[c]	16
Diethyl maleate	U-Ni-A	23	atm.	diethyl succinate	[c]	[d]
Diethyl fumarate	U-Ni-A	23	atm.	diethyl succinate	[c]	[d]
Oleic acid	U-Ni-A	19	atm.	stearic acid	[c]	[d]
Propargyl alcohol	U-Ni-B	25	atm.	*n*-propyl alcohol	[c]	16
Styrene	U-Ni-A	20→56	80	ethylbenzene	90	17
Stilbene	U-Ni-A	20	50	bibenzyl	87	17,18
Tolan	U-Ni-A	24	37	bibenzyl	91	[d]
Mesityl Oxide	U-Ni-A	50-80	80	4-methyl-2-pentanone	83	[d]
Chalcone	U-Ni-A	20	32	1,3-diphenyl-1-propanone	92	[d]

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[a] → indicates a spontaneous rise in temperature.

[b] atm. indicates atmospheric pressure.

[c] In these experiments, the yield of the products were not determined. Absorption of quantitative quantities of H_2 was a measure of 100% hydrogenation.

[d] Unpublished results.

TABLE II. Ring Hydrogenation of Aromatic Compounds

Compound	Catalyst	Temp. (°C)	Pressure (kg/cm^2)	Product	Yield (%)	Ref.
Benzene	U-Ni-BA	90-150	80	cyclohexane	77	17
Benzene	U-Ni-AA	176	[a]	cyclohexane	83	5
Ethylbenzene	U-Ni-BA	100-140	70	ethylcyclohexane	63	17
Styrene	U-Ni-AA	150	[a]	ethylcyclohexane	94	5
Naphthalene	U-Ni-B	120-150	50	tetralin	79	16
Phenol	U-Ni-B	130-150	69	cyclohexanol	80	18
Phenol	U-Ni-BA	185	[a]	cyclohexanol	79	17
Hydroquinone	U-Ni-B	90-150	54	1,4-cyclohexanediol	84	18
Ethyl benzoate	U-Ni-BA	106-150	54	ethyl hexahydrobenzoate	82	17
Diethyl phthalate	U-Ni-BA	114-154	68	diethyl hexahydrophthalate	91	17
Aniline	U-Ni-BA	150-209	96	N-ethylcyclohexylamine[b]	71	17
Aniline	U-Ni-BA	150-215	70	cyclohexylamine[c]	35	17
Acetanilide	U-Ni-BA	120-206	75	N-acetylcyclohexylamine	77	17
Pyridine	U-Ni-BA	150-218	65	piperidine	86	17
Furfural	U-Ni-B	70-160	69	tetrahydrofurfuryl alcohol	76	16

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[a] Vapor phase hydrogenation.

[b] Ethanol solvent, product of reductive alkylation.

[c] Cyclohexane as solvent; dicyclohexylamine isolated in 38% yield.

3.1c. Carbonyl Compounds

At room temperature and at atmospheric pressure, the corresponding alcohols are easily obtained in high yields from aldehydes and ketones with any Urushibara nickel catalyst. However, high pressure reduction at elevated temperatures is the more convenient procedure for preparative purposes. Trace amounts of alkali greatly facilitate the reduction in every case.[19] Under certain conditions, hydrogenolysis of the C-O bonds occurs and the hydrocarbons are obtained with aryl substituted compounds; α-diketones can be selectively reduced to the corresponding acyloins, if the reaction is interrupted after the absorption of one mole of hydrogen.

3.1d. Aromatic Nitro and Nitroso Compounds

Under the proper set of conditions, aromatic nitro compounds are easily reduced to amines. Good yields are obtained easily, provided that no traces of alkali is present in the catalyst. This will thus dictate either the choice of catalyst or the amount of care in preparing it (Table III).

3.1e. Nitriles, Oximes and Hydroxylamines

As is to be expected, secondary amines are always by-products of the reduction of nitriles. Under the proper conditions, the primary amines can be isolated in good yields. Reductions at high temperatures and pressures seem to be preferable (Table IV).

The reduction of oximes resembles that of nitriles, secondary amines being also formed as by-products. Trace amounts of alkali (or ammonia) repress the formation of

TABLE III. Reduction of Aromatic Nitro and Nitroso Compounds

Compound	Catalyst	Temp. (°C)	Pressure[a] (kg/cm^2)	Product	Yield (%)	Ref.
Nitrobenzene	U-Ni-A	80-90	atm.	aniline	97	16
Nitrobenzene	U-Ni-A	80	130	aniline[b]	92	f
Nitrobenzene	U-Ni-A	152	60	aniline[c]	32	f
p-Nitrotoluene	U-Ni-A	64	atm.	*p*-toluidine	90	f
p-Nitroaniline	U-Ni-A	64	atm.	*p*-phenylenediamine	86	f
m-Nitroacetophenone	U-Ni-A	128	70	*m*-aminoacetophenone[b,d]	92	16
m-Nitroacetophenone	U-Ni-A	40-112	63	1-(*m*-aminophenyl)ethanol[b,e]	80	f
p-Nitrosophenol	U-Ni-A	25-30	atm.	*p*-aminophenol	82	f

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[a] atm. = atmospheric pressure

[b] pH: 6-7

[c] pH>10 by adding a small amount of NaOH; 64% of azobenzene isolated.

[d] Time: 120 min.

[e] Time: 200 min.

[f] Unpublished results.

TABLE IV. Reduction of Nitriles and Oximes

Compound	Catalyst	Temp. (°C)	Pressure[a] (kg/cm^2)	Product	Yield (%)	Ref.
Benzonitrile	U-Ni-A	35-38	atm.	benzylamine[b]	78	e
Benzonitrile	U-Co-B	85-90	90-100	benzylamine	85	20
Benzyl cyanide	U-Ni-A	35-38	atm.	phenethylamine[c]	86	e
Benzyl cyanide	U-Co-B	85-90	90-100	phenethylamine	83	20
Adiponitrile	U-Ni-A	35-38	atm.	1,6-hexamethylenediamine	81	e
Adiponitrile	U-Co-B	85-90	90-100	1,6-hexamethylenediamine	85	20
1-Cyclohexenyl-acetonitrile	U-Co-B	85-90	90-100	β-(1-cyclohexenyl)ethyl-amine	80	20
Cyclohexanone oxime	U-Ni-B	25	atm.	cyclohexylamine	--	15
Cyclohexamone oxime	U-Ni-A	80	90	cyclohexylamine	94	21
Benzaldoxime	U-Ni-B	100	75	benzylamine[d]	75	
Acetophenone oxime	U-Ni-A	100	92	phenethylamine	81	21
Benzophenone oxime	U-Ni-A	76	53	benzhydrylamine[c]	98	21

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[a] atm. = atmospheric pressure.

[b] NaOH added and dibenzylamine found in ~ 2% yield.

[c] NaOH added.

[d] KOH added.

[e] Unpublished results.

secondary amines to a great extent (Table IV).

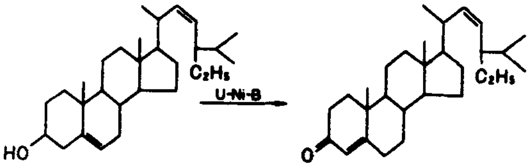
N-benzylhydroxylamine has been reduced to benzylamine in 1 hr over U-Ni-B at moderate temperature and pressure, dibenzylamine being formed in only 5% yield.

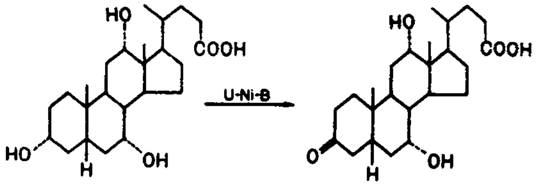
3.2. Hydrogenolysis

The bond between the α-carbon and oxygen of styrene oxide and of β-methylstyrene oxide is cleaved under relatively mild conditions (50-70 kg/cm^2, < 100°) with U-Ni-A. Toluene is the major product of the reduction of benzyl chloride with U-Ni-B, the bibenzyl side-product becoming larger with increasing amount of catalyst. Bibenzyl is the <u>major</u> product of the reduction of benzyl bromide.

3.3. Dehydrogenation

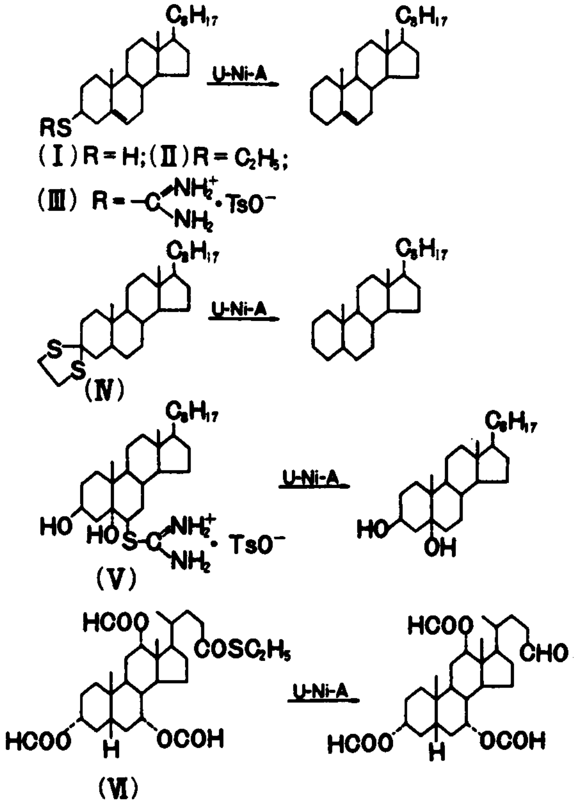
The Urushibara catalysts can also be used as dehydrogenation catalysts. In the presence of U-Ni-B, stigmasterol and cholic acid undergo dehydrogenation to give the corresponding 3-oxo compounds cyclohexanone used as the hydrogen acceptor, is reduced to cyclohexanol.





3.4. Reductive Desulfurization

Several examples of reductive desulfurization in the presence of U-Ni-A of sulfur-containing steroids have been reported. When refluxed with the catalyst in ethanol or



dioxane, the sulfur derivatives I-VI underwent desulfurization. Similarly, the thioacetals of benzaldehyde, acetophenone, and benzophenone gave the hydrocarbons. U-Ni-B did not give good results.

3.5. Other Applications

The Urushibara catalysts sometimes cause N-alkylation.[17] For example, as was described in Table II, N-ethylcyclohexylamine was obtained as the main product when aniline was reduced in ethanol in the presence of U-Ni-BA at 150-200° and under an initial pressure of hydrogen of 75-95 kg/cm^2.

Another characteristic of the U-catalysts is their ability to effect the hydration of nitriles to amides in average to good yields when refluxed in water.[22] The method has the advantage that the reaction may proceed in a neutral medium; U-Ni-B is the best catalyst to effect the hydration. In many cases, hydrogenation occurs also and the amines are obtained as by-products. In other instances, the formation of complexes of nitriles[23] with the catalyst metal was observed.

4. PRECIPITATED METALS AS CATALYSTS

In spite of the earlier observation that the precipitated metals do not catalyze hydrogenation unless activated by digestion with acid or base, it was recently discovered that they do act as catalysts when refluxed in water with various organic compounds.[10] The most favorable mole ratio of water to cyclohexanone (used as standard) is 15:1. The addition of dioxane as a cosolvent permits the reduction of organic compounds which are insoluble in water. The precipitated

TABLE V. Reduction with Precipitated Nickel (Ppt-Ni)[a]

Compound	Wt. (g)	Ni Content of Cat.(g)	Water (ml)	Product	Yield[b] (%)
Styrene	10	4	100	Ethylbenzene	81
Nitrobenzene	10	4	100	Aniline	98
Benzonitrile[c]	10	4	100	Benzylamine[d]	90
3-Cyanopyridine	0.5	1	40[e]	3-Aminomethylpyridine	80
Benzaldehyde	10	4	100	Benzyl alcohol	90
m-Nitrobenzaldehyde	1	2	30[f]	*m*-Toluidine[d]	90
Cyclohexanone	10	4	100	Cyclohexanol[g]	90
Menthone	5	2	40[e]	*exo*-menthol	3
				endo-menthol[h]	1
2-Carbethoxycyclopentanone	1	0.4	10	Ethyl 2-hydroxycyclopentanecarboxylate	71
Acetophenone	8	2	70	1-Phenethyl alcohol	25
				Ethylbenzene	26
Benzophenone	8	2	40[i]	Benzhydrol	31
				Diphenylmethane	40
Mesityl oxide	10	4	100	4-Methyl-2-pentanone[j]	95
Dypnone	1	2	30[f]	1,3-Diphenylbutane	90

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[a] Reduction carried out at reflux for 12 hrs unless specified otherwise; [b] Yields determined by vpc; [c] Time: 20 hrs; [d] Isolated as the hydrochloride salt from the reaction mixture; [e] 20 ml of dioxane as cosolvent; [f] 10 ml of dioxane as cosolvent; [g] Time: 16 hrs; [h] 95% of starting ketone recovered; [i] 30 ml of dioxane as cosolvent; [j] Even after only 5 hrs, the yield was better than 90%.

metals can also be used in hydrogenation with hydrogen at high temperatures and pressures. The major part of this study was carried out with nickel although the other metals exhibited similar catalytic action. An additional advantage of the precipitated metals is that they may be kept (even in air) for a long time and yet retain their activity. A typical procedure for the reduction with precipitated nickel is illustrated by the reduction of styrene and selected examples are given in Table V.[10b]

Reduction of Styrene. A suspension of 10 g of styrene in 100 ml of water was refluxed for 12 hrs in the presence of precipitated nickel containing 4 g of nickel. The solution is filtered hot to remove the nickel which was washed with water and then ether. The aqueous filtrate was extracted with ether and the combined organic phase was dried and evaporated. VPC analysis showed the presence of 81% of ethylbenzene and 19% of styrene.

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