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The Preparation of Raney Nickel Catalysts and their Use Under Conditions Comparable with Those for Platinum and Palladium Catalysts

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It has been the practice in this and many other laboratories to use a platinum or palladium catalyst if a hydrogenation was to be carried out in glass apparatus at room temperatures. However, improvements in the procedure for the preparation of a catalyst from the Raney nickel–aluminum alloy now makes available a catalyst which appears to be approximately as effective as platinum or palladium for catalysis of hydrogenation at pressures of 45 p. s. i. or lower. It is not implied that any of the three metals is lacking in characteristics which make it uniquely useful. For example, the inactivity of palladium against benzenoid nuclei and nitriles and its relative inactivity toward aldehydes make this catalyst particularly useful in certain selective hydrogenations. Platinum and nickel are more alike in activity in that both, under suitable conditions, are effective against almost all types of carbon-to-carbon double bonds, aldehydes, ketones, nitriles, nitro compounds and oximes. Each of them is preferred to the other for certain situations.

The activity of Raney nickel catalysts under mild conditions has been recognized for some time. In our first publication,[2] its effectiveness at low pressure and room temperature was illustrated with results obtained with styrene, acetone, mesityl oxide and acetoacetic ester among other compounds. G. B. L. Smith and his associates[3] have reported on the effectiveness of Raney nickel with and without a platinum promoter particularly for the hydrogenation of nitro compounds. However, it seemed that the Raney nickel catalysts available were not particularly useful at room temperature, except in the hydrogenation of alkene linkages.

The most active nickel catalyst now known to us is one to which we refer as "W-6 Raney nickel."[4] It is made by a procedure given later in this paper. The modifications of earlier procedures consist in rapidly carrying out the removal of aluminum from the Raney alloy at a lower temperature and in washing the catalyst under pressure of hydrogen. The use of hydrogen under pressure in the washing process may be advantageous in that it protects the catalyst from contact with air and the loss of the rather large quantity of hydrogen which is adsorbed on the catalyst.

There is summarized in the table the results of applying the W-6 Raney nickel catalyst to the hydrogenation of a variety of organic compounds. The hydrogenations were carried out in glass under the conditions normally used with platinum and palladium catalysts. The absorption of hydrogen was in every experiment within ±4% of that required for the formation of the compounds reported in the last column of the table. Except as noted under the table the hydrogenations went quantitatively to a single product.

Compounds containing a carbon–carbon double bond such as cinnamic acid, ethyl cinnamate and diethyl isopropylidenemalonate, were very rapidly hydrogenated in three to ten minutes to the corresponding saturated compound. Stearolic acid was converted into elaidic acid within less than two minutes. The elaidic acid was then much more slowly converted to stearic acid. Thus it is possible with the W-6 catalyst to selectively hydrogenate an alkyne to an alkene linkage.

Representative aldehydes and ketones were rapidly hydrogenated to the corresponding alcohols. It was found that the addition of a little triethylamine to the reaction mixture approximately cut in half the time required for the hydrogenation of an aldehyde or ketone. Thus through the use of W-6 catalyst with triethylamine all of the aldehydes and ketones tested were hydrogenated to the corresponding alcohol within less than forty minutes, while some of them reacted much more rapidly. The presence of triethylamine retards the hydrogenation of a benzenoid nucleus so that even with a naphthyl ketone there is no danger of hydrogenating the nucleus.

The W-6 catalyst is not only effective against alkene, alkyne and carbonyl linkages, but will also bring about the hydrogenation of benzenoid and pyridinoid nuclei. Diphenyl, hydroquinone, β-naphthol, methyl β-naphthylcarbinol and β-phenylethanol were hydrogenated although more slowly than the types of compounds referred to just above. However, as is shown in the case of hydroquinone, the rate of hydrogenation can be greatly increased through the use of higher ratio of catalyst to compound undergoing hydrogenation. The hydrogenation of the pyridinoid ring in quinoline went rapidly. The hydrogenation of the compounds containing two unsaturated rings was selective, in that under the conditions used only one ring was hydrogenated. The W-6 catalyst was also effective in bringing about a hydrogenolysis of benzhydrol, but not without hydrogenation.

The W-6 catalyst was effective in catalyzing the hydrogenation of nitriles such as benzyl cyanide and stearonitrile. The proportion of primary and secondary amine produced from benzyl cyanide was similar to that observed in a high

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[1] Monsanto Chemical Co. Fellow, 1946–1947.

[2] Covert and Adkins, THIS JOURNAL, **54**, 416 (1932).

[3] Smith, Scholnik, Reasenberg and Lieber, *ibid.*, **63**, 1192 (1941).

[4] For references and designation of catalysts see Adkins and Pavlic, *ibid.*, **69**, 3040 (1947).

pressure hydrogenation in the absence of ammonia. However, there was no secondary amine formation in the hydrogenation of stearonitrile.

p-Nitrotoluene was converted smoothly and rapidly into *p*-toluidine of excellent quality. The reduction of a nitro group is so exothermic a reaction that precautions must be taken to keep the reaction under control. This is particularly important when a catalyst so active as W-6 is used. As indicated below, there is danger in the use of W-6 Raney nickel under certain circumstances.

The oximino groups in a simple oxime, in an oximinoketone and in an oximinoketo ester were smoothly and rather rapidly hydrogenated to the primary amine group. The keto groups were also hydrogenated to alcohol groups, but the carboethoxy group was stable at the low pressure. Under higher pressure, as will be described in a later paper, the W-6 catalyst catalyzes the conversion of carboethoxy to carbinol.

An alkaline catalyst, referred to as W-7 Raney nickel, has given good results in hydrogenating

TABLE I

HYDROGENATIONS WITH W-6 NICKEL CATALYSTS[a]

Compound, g.	Time Hr.	Time Min.	Product
13.0 Ethyl acetoacetate	1	10	Ethyl β-hydroxybutyrate, b. p. 77–78° (15 mm.), n^{25}_{D} 1.4200, d^{25} 1.0052
13.0 Ethyl acetoacetate[b]	0	34	Ethyl β-hydroxybutyrate
9.1 Benzophenone	0	17	Benzohydrol needles, m. p. 66–69°, phenylurethan, m. p. 138–140°
9.1 Benzophenone[b]	0	8	Benzohydrol
8.5 β-Acetylnaphthalene[b]	0	25	Methyl-β-naphthyl carbinol, needles, m. p. 67–68.5°, b. p. 125–128 (2 mm.); phenylurethan, m. p. 143.5–144.5°
6.6 Cinnamaldehyde[b]	0	39	3-Phenyl-1-propanol, b. p. 82–84° (1 mm.), n^{25}_{D} 1.5354
6.0 Acetophenone	0	22	Methyl phenyl carbinol, b. p. 103-104° (20 mm.), n^{25}_{D} 1.5251; phenylurethan, m. p. 93–94°
6.0 Acetophenone[b]	0	10	Methyl phenyl carbinol.
5.3 Benzaldehyde	0	26	Benzyl alcohol, b. p. 104–105 (20 mm.), n^{25}_{D} 1.5340; phenylurethan, m. p. 74–76°.
5.3 Benzaldehyde[b]	0	12	Benzyl alcohol, b. p. 104-105° (20 mm.), n^{25}_{D} 1.5340
5.0 *n*-Hexaldehyde	1	50	*n*-Hexyl alcohol, b. p. 67–69° (20 mm.), n^{25}_{D} 1.4134, phenylurethan, m. p. 40-42°
5.0 *n*-Hexaldehyde[b]	0	40	*n*-Hexyl alcohol
5.8 Acetone	0	38	Isopropyl alcohol
5.8 Acetone[b]	0	23	Isopropyl alcohol
8.8 Ethyl cinnamate	0	3	Ethyl β-phenylpropionate
7.4 Cinnamic acid	0	10	β-Phenylpropionic acid
7.0 Stearolic acid	2	0	Stearic acid, m. p. 67–70°, b. p. 188-190° (1 mm.)
7.0 Stearolic acid	0	2	Elaidic acid, m. p. 42-45°, b. p. 185-187° (1 mm.)
10.0 Diethyl isopropylidene malonate	0	8	Diethyl isopropylmalonate, b. p. 74–76° (3 mm.), n^{27}_{D} 1.4186; acid, m. p. 86.5–87.5°
5.2 Diphenyl[c]	6	0	Phenylcyclohexane, b. p. 125–128° (30 mm.), n^{25}_{D} 1.5210
5.5 Hydroquinone	36	0	1,4-Cyclohexanediol, needles, m. p. 98.5–101°[d]
5.5 Hydroquinone[c]	8	0	1,4-Cyclohexanediol
6.1 β-Phenylethanol[c]	96	0	β-Cyclohexylethanol, b. p. 118–120° (36 mm.), n^{25}_{D} 1.4700; phenylurethan, m. p. 119.5–120.5°
7.2 β-Naphthol	4	0	1,2,3,4 - Tetrahydro - 2-naphthol (27%), b. p. 118–120° (3 mm.), insoluble in alkali. 5,6,7,8 - Tetrahydro - 2-naphthol (55%), b. p. 114–116° (3 mm.), soluble in alkali
9.2 Diphenylcarbinol	27	0	{Diphenylmethane Benzylcyclohexane} b. p. 90-100° (3 mm.), n^{25}_{D}, 1.5600[e]
8.5 β-Acetylnaphthalene	45	0	Methyl - β - tetrahydronaphthylcarbinol[f]
5.9 Benzyl cyanide	1	6	β-Phenethylamine (72%), b. p. 106–107° (37 mm.), n^{25}_{D} 1.5306; picrate, m. p. 173–174° Di-(β-phenethyl) amine (15%), b. p. 215–220° (38 mm.), n^{25}_{D} 1.5521; picrate, m. p. 150–151.5°
6.7 Stearonitrile	5	0	*n*-Octadecylamine, b. p. 146–154° (2 mm.), m. p. 51.5–53°; picrate, m. p. 116°; hydrochloride, m. p. 159–161°
6.9 *p*-Nitrotoluene	0	13	*p*-Toluidine, b. p. 107–109° (33 mm.), m. p. 43–44°; picrate, m. p. 179.5–180.5° (dec.)
5.7 Cyclohexanone oxime	0	45	Cyclohexylamine (90%), b. p. 48–52° (30 mm.), n^{25}_{D} 1.4569; hydrochloride, m. p. 204–206°
8.2 α-Oximinopropiophenone	3	30	2 - Amino - 1 - phenyl - 1-propanol, m. p. 99–103°; hydrochloride, m. p. 189–191°; oxalate, m. p. 243–244.5°[g]
8.0 Ethyl α-oximinoacetoacetate	1	20	Ethyl α-amino-β-hydroxybutyrate, b. p. 82–84° (2 mm.), n^{25}_{D} 1.4495[h]
6.5 Quinoline	0	50	1,2,3,4 - Tetrahydroquinoline, b. p. 85–86° (2 mm.), n^{25}_{D} 1.5910; hydrochloride, m. p. 179–181°

[a] The hydrogenations were carried out at room temperature (25–30°) under a pressure of 15 to 45 p. s. i. in a 250-ml. glass centrifuge bottle shaken at 172 r. p. m. The reaction mixture was made up to a volume of 100 ml. with dry ethanol and contained 2 g. of W-6 Raney nickel, except as noted below. [b] The reaction mixture contained 2 ml. of triethylamine. [c] Nine grams of W-6 Raney nickel was used. [d] Other work has shown the product to be a mixture of the *cis* and *trans* isomers in approximately equal proportions. [e] This value indicates approximately three parts of diphenylmethane and one part benzylcyclohexane. [f] The compound is an alcohol, b. p. 119–119.5° (2 mm.), n^{25}_{D} 1.5484, $d^{25°}$ 1.0408, M_{R} calcd. 53.33, found 53.3. Phenylurethan, m. p. 230–231.5°. *Anal.* Calcd. for $C_{12}H_{16}O$: C, 81.8; H, 9.14. Found: C, 81.6; H, 9.08. The position of the hydrogens added is not known. [g] A mixture of stereoisomers. [h] The yield of a mixture of stereoisomers was low, probably because of the formation of a piperazine during distillation of product.

ketones, phenols and nitriles, for which alkali in the reaction mixture is beneficial.[5,6] The catalyst is attractive because of the simplicity of the procedure used in washing it. It was somewhat less active than W-6 toward diphenyl and benzyl cyanide, but the proportion of primary to secondary amine was increased. The W-7 catalyst was somewhat more active toward acetophenone than W-6 without triethylamine. The catalyst was remarkably active toward hydroquinone, giving complete hydrogenation within fifteen minutes instead of in eight hours as with W-6.

Preparation of W-6 Raney Nickel Catalyst

WARNING.—The Raney nickel catalysts described below have given reactions proceeding with violence. In one case a hydrogenation proceeding at 125° at 5000 p. s. i. showed a pressure rise to considerably more than 10,000 p. s. i. before the reaction could be stopped or the pressure released. Several instances of sudden increases in pressure have been noted when quantities of catalyst of the order of 10 to 15 g. were being used in the temperature range of 100 to 150° under 5,000 p. s. i. The high activity of the catalysts and the presence of aluminum and rather large amounts of adsorbed hydrogen make it advisable to be *very cautious in their use.* No difficulty has been encountered at temperatures below 100°. Hydrogenations may be carried out safely above 100° if the ratio of catalyst to possible reactants is kept low, *e. g.*, 5% as much nickel as weight of hydrogen acceptor.

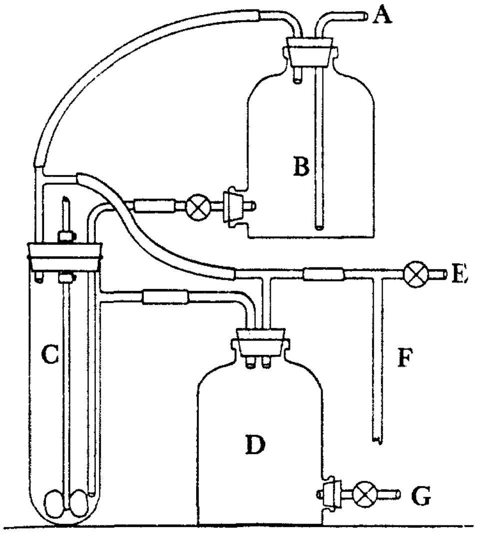

Fig. 1.—Apparatus for washing catalyst: A, distilled water inlet; B, reservoir for distilled water; C, chamber for washing catalyst; D, overflow bottle; E, hydrogen inlet; F, manometer; G, water outlet. It is more convenient to have the inlet tube for wash water sealed into the bottom of the chamber rather than introduced through the stopper as shown.

Procedure.—In a two-liter Erlenmeyer flask equipped with a thermometer and a stainless steel stirrer, is placed 160 g. of sodium hydroxide in 600 ml. of distilled water. The rapidly stirred solution is allowed to cool to 50° in an ice-bath equipped with an overflow siphon. Then 125 g. of Raney nickel–aluminum alloy is added in small portions over a period of twenty-five to thirty minutes. The temperature is maintained at 50 ± 2° by controlling the rate of addition of alloy to the sodium hydroxide and of ice to the cooling bath. When all the alloy has been added, the suspension is digested at 50° for fifty minutes with gentle stirring. It is usually necessary to remove the ice-bath and replace with a hot water-bath. The catalyst, after digestion, is washed three times by decantation and then transferred immediately to the washing tube for further washing.

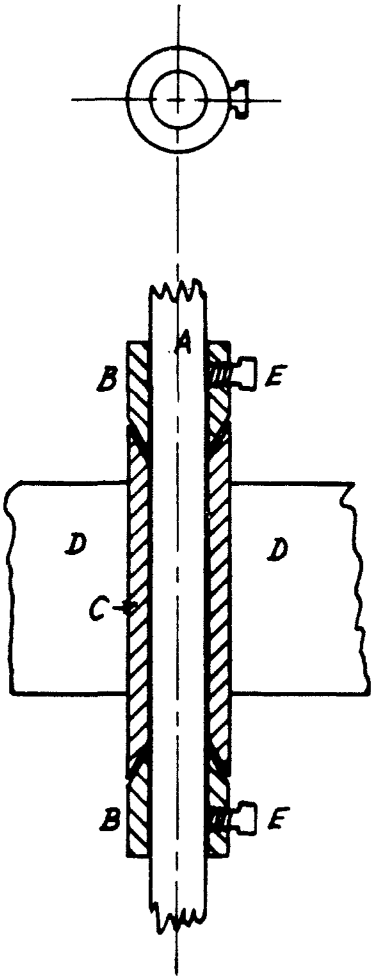

Fig. 2.—Gas tight bushing: The gas tight bushing for the shaft of the stirrer consists of three parts; two cones (B) which fit the shaft snugly and are attached to it by set screws (E); and a bushing (C) so cut that the cones fit into it at top and bottom. The two cones are placed on the 0.25 inch shaft (A) of the stirrer, above and below the bushing and attached to the shaft so that they fit snugly against the bushing. A gas-tight seal is obtained by placing a drop or two of heavy lubricating oil between each cone and the bushing. The over-all dimensions of the bushing are approximately 13 × 65 mm. and it is held in a rubber stopper (D).

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(5) Delépine and Horeau, *Compt. rend.*, **201**, 1301 (1935).

(6) Flichaire and Chambert, *Bull. soc. chim.*, **11**, 22 (1944).

A glass test-tube, approximately 5.1 cm. in diameter and 38 cm. in length, with a side arm 6 cm. from the top, is used as the container in washing the catalyst. The tube is equipped with a snugly fitting rubber stopper which is held in place by a suitable device. The stopper carries a gas tight bushing (Fig. 2) through which the 0.25-inch shaft of a stainless steel stirrer projects to the bottom of the washing tube. A 5-liter reservoir for distilled water is so placed that water will flow from it through a stopcock down a glass tube, 8 mm. in diameter, which passes through the stopper and down the side of the washing tube to its bottom. The side arm of the test-tube is connected by rubber tubing to a 5-liter overflow bottle from which the water may be allowed to flow through a stopcock to the drain. A connection from a source of distilled water is made to the reservoir. All connections of rubber and glass tubes should be so fastened that they will withstand the pressures used. The general arrangement of the apparatus is shown in Fig. 1, while certain details of construction are given in Fig. 2.

The catalyst sludge is immediately transferred to the washing tube after the third decantation. The last portions are rinsed from the flask into the tube with distilled water and the tube and reservoir nearly filled with distilled water. The apparatus is then rapidly assembled, and hydrogen introduced so that the water in the reservoir, washing tube and overflow bottle is under a pressure about 0.5 atm. above that of the outside atmosphere. The stirrer is operated at such a speed that the catalyst is suspended to a height of 18–20 cm. Distilled water from the reservoir is allowed to flow through the suspended catalyst at a rate of about 250 ml. per minute. When the reservoir is nearly empty and the overflow bottle full, the drain cock and distilled water inlet are simultaneously opened to an equal rate of flow such that, as the overflow bottle empties, the reservoir is filled, while the pressure in the system remains constant.

After about 15 liters of water has passed through the catalyst, the stirrer and the water are stopped, the pressure released and the apparatus disassembled. The water is decanted from the settled sludge, which is then transferred to a 250 ml. centrifuge bottle with 95% ethanol. The catalyst is washed three times by stirring, not shaking, with 150 ml. of 95% ethanol, centrifuging after each addition. In the same manner, the catalyst is washed three times with absolute ethanol. One to two minutes centrifugation at 1500–2000 r. p. m. is sufficient to separate the catalyst. All operations should be carried out as rapidly as possible if a catalyst of the maximum activity is desired. The catalyst should be stored in a refrigerator in a closed bottle filled with absolute ethanol. The total elapsed time from the beginning of the addition of the alloy to the completion of the preparation, with the catalyst in the refrigerator, should be not more than about three hours.

The volume of the settled catalyst in ethanol is about 75–80 ml. containing about 62 g. of nickel and 7–8 g. of aluminum. It amounts to about twenty-eight "half teaspoonsful" if it is so measured. The catalyst loses some of its special activity upon standing, but seems to be quite active for about two weeks when stored in a refrigerator. After this period it is similar in activity to the Raney nickel made by earlier procedures. The W-3 to W-7 catalysts all lose their special activity rather rapidly when stored under water.

The procedure for the preparation of W-5 Raney nickel, a somewhat less active, but nevertheless excellent catalyst, is the same as that for W-6, except that it is washed at atmospheric pressure without the addition of hydrogen to the system. The W-5 catalyst is similar in method of preparation and activity to the W-4 Raney nickel catalyst as prepared by Pavlic.[4,7] The procedure in the preparation of W-7 Raney nickel, after the digestion and the three decantations, is to transfer the catalyst to a 250 ml. centrifuge bottle with 95% alcohol. It is then washed three times by stirring, not shaking, with 150 ml. of 95% ethanol, centrifuging after each addition. In the same manner, the catalyst is washed three times with absolute ethanol.

Summary

A procedure has been described for the preparation of Raney nickel catalysts, which are useful at room temperatures and low pressures, for the catalysis of the hydrogenation of alkyne and alkene linkages, aldehydes, ketones, nitro compounds, nitriles, oximes and benzenoid and pyridinoid nuclei. While the amount of catalyst required for a given rate of hydrogenation is higher than for platinum and palladium catalysts, it appears that a properly prepared Raney nickel catalyst is effective under as mild conditions of temperature and pressure as are the noble metals. It appears that, under the conditions normally used for the platinum and palladium catalysts, the W-6 Raney nickel catalyst is more selective in action than at higher pressures and temperatures. For example, stearolic acid was converted within two minutes to elaidic without significant reduction of the latter to stearic acid. It has been found that the addition of a small amount of triethylamine to a reaction mixture markedly increases the rate of hydrogenation of aldehydes and ketones over Raney nickel.

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[7] Pavlic and Adkins, THIS JOURNAL, 68, 1471 (1946).