CATALYTIC HYDROGENATION USING RANEY NICKEL

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In industry and in research institutions catalytic hydrogenations have become indispensable processes. Leaving out of consideration mixtures of catalysts, such as mixtures of vanadium, molybdenum, chromium, and other oxides, we are left with the somewhat expensive platinum and palladium catalysts, or the inexpensive nickel (*1a–e*). It has been found that the poor relation, nickel, is an extremely versatile catalyst, and is well adapted for use not only in research, but as a practical tool in teaching the technique of catalytic hydrogenation to students. The paper now presented has been written with this latter purpose in mind.

Nickel may be prepared in active form by several processes. The earliest one was discovered (1897) by Sabatier and Senderens (*1a*). In this process, pumice or other porous support is soaked in a solution of a nickel salt, *e. g.*, nickel nitrate, which is then converted by alkalies or direct heating into nickel oxide. This is reduced by means of hydrogen at 300° to 450° to an active finely-divided, pyrophoric form of nickel. The original method suffered from the drawback, at least on the laboratory scale, that hydrogenations were performed in heated tubes; the compounds to be hydrogenated being vaporized and passed with hydrogen over the heated nickel. This drawback is not a radical one, since this type of catalyst has been extensively used in liquid phase experiments.

RANEY NICKEL

In 1927 Murray Raney introduced a vastly more convenient and amenable form of nickel catalyst (*2*). He treated alloys of nickel and aluminum with sodium hydroxide solution; the aluminum dissolved to form aluminate leaving a black residue of finely-divided nickel. This residue possessed the advantage that it is readily settled, could therefore be easily washed with water by decantation, without filtration, and, after washing with ethanol to remove water, could then be used as a suspension in alcohol. Adkins and his collaborators have greatly improved the quality and performance of Raney nickel by attention to details in its preparation. They have thus produced nickel of several comparatively well-defined grades of activity—that of highest activity (later referred to as W-6 Raney nickel (*3d*)) comparing well in range of applicability, and often of specificity, with the different grades of active platinum and palladium obtainable.

The first of the improved forms, prepared by Covert and Adkins (*3a*), was not particularly active. But Pavlic and Adkins (*3b*) produced a much more active one by lowering the temperature (to 50°) at which the nickel–aluminum alloy was treated with alkali, shortening the period of this treatment (from 12 to $1^1/_2$ hours), and preventing undue contact of catalyst with air during washing. Adkins and Pavlic (*3c*) designated this method as W-4; and later, Adkins and Billica (*3d*) prepared the most active of these Raney nickel catalysts (W-6) by maintaining a pressure of hydrogen over the nickel throughout washing operations. They furthermore (*3e*) investigated the effect of temperature and other factors on rate of hydrogenation. The author finds, however, that Raney nickel W-4, as prepared by Adkins and Pavlic (*3b*, *3c*), is excellent. It is this method which, with a few simplifications, will now be described.

PREPARATION OF RANEY NICKEL CATALYST

Sodium hydroxide (65 g.) and water (250 ml.) are placed in a conical flask (1 liter) fitted with thermometer and stirrer (which may be of nickel, steel, tantalum, etc., twisted as recommended by Hershberg (*4*)). The flask is immersed in an easily removable bath of cold water. When the temperature of the stirred solution has fallen to 50° Raney nickel–aluminum (50 per cent) alloy (50 g.) is added in small portions (2 to 5 g.) at such a rate that the temperature remains at 50°±2°, the mixture being meantime rapidly stirred. If the temperature falls too low the cooling bath should be removed until 50° is again attained. The whole amount of the alloy should have been added by the end of half an hour. The cooling bath is now removed, and the mixture kept at 50°, using a hot-water bath, for 50 minutes, with gentle stirring. The stirrer is stopped, the mixture allowed to cool, and when the nickel has settled, the supernatant liquid is poured off, and the residue washed once by decantation with distilled or boiled-out tap water, avoiding contact of the nickel with air by swirling suspensions rather than by shaking. The nickel is now swirled into a 500-ml. measuring cylinder which is then filled with water. The nickel is washed in this water by mechanical or manual stirring. After settling, the supernatant liquid is syphoned off through a glass U-tube, which has first been filled with water to initiate syphoning, or by gentle suction at the pump. The washing operation is repeated until the syphoned liquor is free from alkali (neutral to litmus). The resi-

due is now washed similarly, two or three times, with ethanol (100 ml. at a time). Finally the whole volume (catalyst + ethanol) is made up to 125 ml., the mixture swirled, and rapidly decanted into a reagent bottle. Much of the heavier portion of the nickel which does not decant with the ethanolic suspension may be rapidly scraped by means of a spatula into the reagent bottle. After allowing the nickel to settle, the supernatant liquid is poured back into the measuring cylinder, the residue of nickel swirled into suspension, and the whole decanted into the reagent bottle; this procedure being repeated until all the nickel has been transferred. Throughout, every effort must be made to prevent undue mixing with air. The well-mixed suspension thus prepared should contain approximately 25 g. of nickel (from 50 g. of 50 per cent alloy) in 125 ml. of ethanolic suspension, *i.e.*, 1 g. of nickel in 5 ml. of suspension.

Caution! Raney nickel when *dry* ignites spontaneously in air—it is pyrophoric—and must therefore be kept always "wet" with liquids such as ethanol or water. The used nickel must never be thrown into a waste bin, but poured down the special waste drain. I have found that for small quantities washing down the sink with plenty of water has given no trouble.

MEASURING RANEY NICKEL

Since Raney nickel is pyrophoric it is not possible to weigh it. It is always necessary to "measure" it in suspension, *e.g.*, by means of a spoon of known capacity. The writer has found the following method very satisfactory.

The neck of the reagent bottle containing nickel + ethanol is fitted, as shown in Figure 1, with a cork or

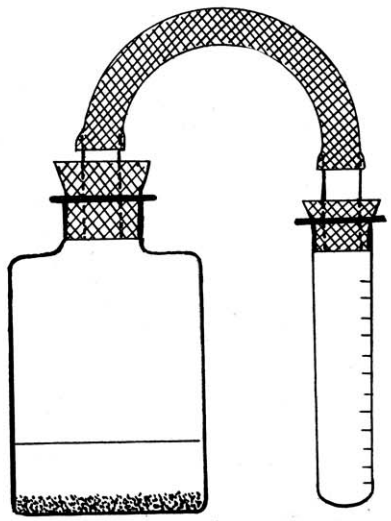


Figure 1

rubber stopper through which passes a wide glass tube (1 cm. in diameter and 5 cm. long), one end being flush with the inner end of the cork, and the other having a length (12 cm.) of wide rubber tubing attached to it. The tubing is further fitted to a glass tube + cork + test tube, as above described for the bottle. The test tube is calibrated with 5 ml. graduations. Suspensions of nickel are measured out thus: The nickel-ethanol suspension is swirled until thoroughly mixed, then the bottle is suddenly inverted, and the suspension shot into the test tube. If too much has been transferred the operation is carried out in reverse. In each operation care must be taken to insure that heavy particles of nickel have a good chance of being transferred. The test tube is now detached, the suspension transferred to the hydrogenation flask, residual nickel being scraped in with a spatula, and finally rinsed in with the minimum volume of fresh ethanol.

Note 1. In order to remove catalyst poisons, before use all rubber parts should be soaked in dilute caustic alkali solution, then in nickel–ethanol suspension, and rinsed with ethanol.

Note 2. The ethanol used in all these and actual hydrogenation processes must be free from catalyst poisons and from impurities which may react with hydrogen. To remove these it is strongly recommended that the ethanol be mixed with a portion of the nickel suspension for about 15 minutes, then decanted—the used nickel being, of course, discarded. As an additional precaution the ethanol may be distilled from fresh nickel, but this is unnecessary.

Note 3. Substances being hydrogenated should be pure or at least free of catalyst poisons, *e.g.*, sulfur compounds.

THE HYDROGENATION APPARATUS

Hydrogen may be obtained from a cylinder but should be purified. It has been found that hydrogenations which could not be effected, or at best extremely slowly, using palladium or platinum catalysts and cylinder-hydrogen, could be carried out with pure hydrogen as generated by the author's hydrogen (and air-free carbon dioxide) generator (*5*). The hydrogen is generated by the action of 1:1-hydrochloric acid solution on pure (at least arsenic-free) zinc which has been treated *in situ* with 3 per cent copper sulfate solution to form the zinc–copper couple. The gas is passed through two bubblers containing (1) mercuric chloride solution, (2) alkaline potassium permanganate solution; it is of no advantage to dry the hydrogen. The hydrogen is collected in a 320-ml. measuring tube (Figure 2, *A*), and can be transferred, by suitable adjustment of the three-way tap, *B*, and raising the water reservoir, *C*, to flush out and finally fill the hydrogenation flask, *D*.

Rubber connections should be treated as described earlier. A layer of castor oil smoothed over the outside of the rubber tubing is rapidly absorbed, and is alleged to form eventually within the rubber a plastic film which offers resistance to diffusion of gases.

Stirring of the suspension in *D* is effected by the excellent method of Noller and Barusch (*6*) using a rotating magnet, *E*, actuated by a rotating Alnic permanent magnet, *F*. The former, *E*, of the shape shown (enlarged in Figure 2) is easily made by sealing and flattening the end of a thick-walled pyrex glass tube, blowing

the bulb and allowing to cool. A decapitated, soft-iron nail is inserted, and the open end of the glass tube sealed and flattened—at right angle to the other flattened end. This stirrer rotates on a point on the surface of the bulb, and operates with the minimum of friction and noise. Small bulbs instead of flattened ends are just as effective.

The Alnic magnet is preferably mounted on a bearing, and belt-driven by a motor controlled by an adjustable resistance.

THE PROCESS OF HYDROGENATION

The first requirement is to saturate the catalyst (*cf.* 6). To this end, the nickel–ethanol suspension is introduced into the flask *D*, using 5 ml., *i.e.*, approximately 1 g. of nickel for every gram of substance to be hydrogenated. This is relatively a very large excess of catalyst, much less may safely be used, but an excess ensures maximum contact area of catalyst and consequent enhancement in speed of reaction. The stirrer, *E*, is inserted, the ground-joints of *D* and the thistle-funnel *G* greased thinly with vaseline or silicone grease, and, although not essential, *G* is wired or clamped to *D*. The author finds that a suitable clamp is readily made by attaching springs at four points on the periphery of a flat brass ring which presses against the base of the flask *D*, the springs being looped over the stopcock *H*. Obviously, the brass fitting can be dispensed with if the flask *D* is provided with the well-known glass hooks. The flask is now flooded several times with hydrogen—it is dangerous to evacuate a thin-walled conical flask—by suitable manipulation of taps *B* and *H* and by raising and lowering the reservoir *C*. With *B* set to connect *A* and *D*, the reservoir *C* is raised so as to develop the highest possible water pressure (as indicated in Figure 2), and the stirrer set in motion. When absorption of hydrogen ceases (in approximately an hour) the stirrer is stopped, the reservoir, *C*, lowered to below the level of the water in the graduated tube *A*, the ethanolic solution of the substance to be hydrogenated, or even a suspension of the substance, is then poured into the funned *G*, and sucked into the reaction flask *D* after opening the tap *H*. Obviously, air must not be allowed to enter during this operation. Residual solution is washed in by use of fresh ethanol. After the usual leveling of water surfaces in *C* and *A* the volume in *A* is read, *C* raised, the stirrer set in motion, and absorption allowed to continue until complete. *A* may, of course, be refilled with hydrogen, during reaction, if required. After releveling, the volume in *A* is again used. Hence the volume of hydrogen (moist) absorbed under the observable temperature and pressure is found: this volume is reduced to S.T.P. The funnel *G* is then disconnected from the flask *D*, the neck of *D* wiped free of grease, the suspension filtered through a sinter-glass filter, the nickel boiled several times with fresh ethanol to remove the hydrogenated product, which often remains tenaciously attached to the catalyst, and the united filtrates distilled to dryness. The product which is invariably nearly pure may then be crystallized from a suitable solvent, or, if a liquid, distilled.

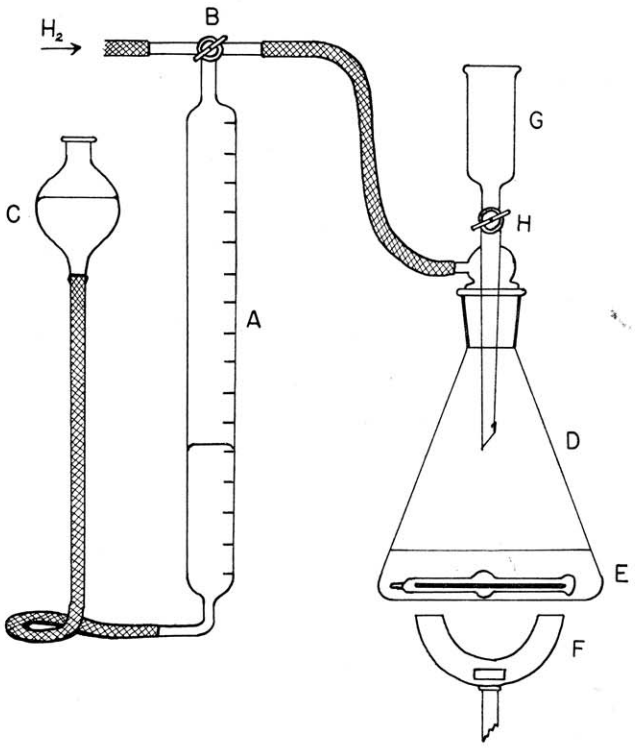


Figure 2

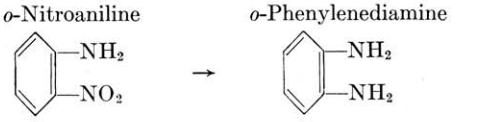
Note: (1) The residual nickel must not be allowed to become dry and free of ethanol: it may often with advantage be used again. (2) All ethanol used must have been pretreated with nickel catalyst: it too, after recovery, is the ideal solvent for the next hydrogenation. (3) Dioxane, ethyl acetate, methanol, and even acetone may also be employed as solvents, but it must be remembered that acetone is slowly reduced under the experimental conditions to sec-propyl alcohol. (4) The solution of the substance being hydrogenated must be at room temperature, and show no tendency to crystallize, otherwise crystallization will take place on the surface of the nickel, and completely prevent hydrogenation. For this reason if the substance is relatively insoluble in ethanol it is advisable to wash it in solid condition into the flask *D*.

EXPERIMENTAL

The following examples of catalytic hydrogenation have been selected to provide students with varied experience in the hydrogenation process, and because of their intrinsic interest. The examples have been carefully selected to ensure that the product is a solid of markedly different color or melting point from the starting material, and is of such a nature that an interesting and characteristic derivative may be prepared to establish its identity. For these reasons the examples given by Covert and Adkins (*3a*), styrene (→ethylbenzene), acetone (→sec-propyl alcohol), mesityl oxide (→methyl isobutyl ketone→methyliso-

butylcarbinol), have not been included, since the products are liquid, although they can be readily converted into characteristic derivatives.

(*A*) *Reduction of a Nitro Derivative.*

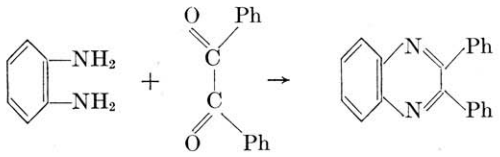


In the reduction of a nitro to an amino compound six atoms of hydrogen are required ($RNO_2 + 6H \rightarrow RNH_2 + 2H_2O$). Hence, for the reduction of 1 g. mol of *o*-nitroaniline (138 g.), 3 g. mols of hydrogen (3 × 22,400 ml. at N.T.P.) will be required.

Nickel–ethanol suspension (15 ml. containing ~3 g. nickel) washed in with ethanol (10 to 15 ml.) was saturated with hydrogen in half an hour. Ortho-nitroaniline (4.14 g.; 0.03 g. mol) in powdered form was rinsed into the hydrogenation flask with ethanol (25 ml.). In three hours absorption of hydrogen was at an end—1765 ml. were absorbed; theory requires 2016 ml. During this time the orange-colored solution became nearly colorless. The reaction mixture was filtered, the nickel thoroughly extracted by boiling with ethanol, and the combined filtrates distilled to dryness, assisted at the end by evacuation. The residue was at once extracted with boiling benzene, in which *o*-phenylenediamine is very soluble in the hot but not very soluble in the cold. On cooling, the solution deposited pale brown plates which, by crystallization once from petroleum (b. p. 80–100°), gave colorless, nacreous leaflets, m.p. 99–100° (2.77 g.; theory requires 3.24 g.; yield 86 per cent). Ortho-phenylenediamine also crystallizes beautifully from methylene dichloride in diamond-shaped crystals.

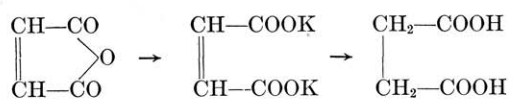
In another experiment, using another preparation of Raney nickel, *o*-nitroaniline (1.38 g.) absorbed hydrogen (650 ml. at N.T.P.; theory requires 672 ml.) in 45 minutes, and gave *o*-phenylenediamine (0.90 g.; yield 83 per cent).

Derivative.



The product may be identified by preparation of 2,3-diphenylquinoxaline; a solution of *o*-phenylenediamine (1.08 g.) and benzil (2.10 g.) in ethanol was boiled for 5 minutes. On cooling, colorless needles separated, and after crystallization from methanol had m. p. 122° to 123° (literature, 126°).

(*B*) *Hydrogenation of Maleic Acid.*



Maleic acid which has been kept contains fumaric acid, and the latter takes up hydrogen extremely slowly, much more slowly than maleic acid does; it is characteristic that *cis* isomerides hydrogenate more rapidly than the *trans* isomerides do. Accordingly, the expedient was adopted of hydrogenating potassium (or sodium) maleate, prepared *in situ* by dissolving maleic anhydride in water, adding ice-cold potassium hydroxide solution until alkaline, and hydrogenating the maleate to the succinate ion. Acidification gave succinic acid.

Thus, maleic anhydride (chipped from a crystalline block, 1.96 g.; 0.02 g. mol) was dissolved in cold water (10 ml.). An ice-cold 15 to 20 per cent solution of potassium hydroxide was added until the mixture was slightly alkaline to litmus. This was added to the previously hydrogen-saturated nickel (2 g. of nickel in 10 ml. of ethanol to which 10 ml. of water had been added), and hydrogenated. In three hours hydrogenation was practically complete (340 ml.; theory requires 448 ml., possibly absorption had occurred to some extent during initial mixing of reactants). The filtered solution was rendered strongly acid by means of concentrated hydrochloric acid, and then evaporated to dryness on the water bath. The residue was extracted by boiling several times with ethanol, filtering from the insoluble potassium chloride, evaporating the ethanolic solution, and crystallizing the residue from methyl cyanide or from the minimum amount of water. There is considerable loss when water is used. The succinic acid so obtained (1.72 g.; yield 73 per cent) softened at 175°, and melted at 182–185°, (literature, 184–185° and 189–190°, *cf.* 7).

(*C*) *Hydrogenation of Chalcone* (*Benzylideneacetophenone*).

$$PhCH{=}CH{-}COPh\ (I) \rightarrow PhCH_2{-}CH_2{-}COPh\ (II)$$
$$\rightarrow PhCH_2{-}CH_2{-}CH(OH)Ph\ (III)$$

(1) Hydrogenation of chalcone, (I), to benzylacetophenone, (II).

Nickel (~ 2 g.) recovered from other hydrogenation experiments was thoroughly washed with water until free from alkali, then washed with ethanol and finally with ethyl acetate. It was suspended in pure ethyl acetate (5 ml.) and saturated with hydrogen. Chalcone (2.08 g.; 0.01 mol) in ethyl acetate (5 ml.) was added and washed in with more solvent (10 ml.). Absorption of the amount of hydrogen theoretically required (224 ml., N.T.P.) for hydrogenation of (I) → (II) was accomplished in 5 minutes. The filtered, evaporated solution gave a white solid (1.79 g.; yield 85 per cent) which, after crystallization from methanol, had m. p. 69–70° (literature, 72–73°). (Strauss and Grindel (*8a*) used palladium, and Adams (*8b*) used his platinum catalyst for this hydrogenation, with similar results.)

Derivative. The 2,4-dinitrophenylhydrazone of benzylacetophenone was prepared by adding a drop of concentrated sulfuric acid to a suspension of 2,4-dinitrophenylhydrazine in methanol, then adding the clear solution so obtained to a solution of the ketone in hot methanol. The hydrazone separated at once as an orange precipitate, and was dissolved in ethyl acetate

from which it crystallized in prisms, m. p. 180° (*cf. 9*).

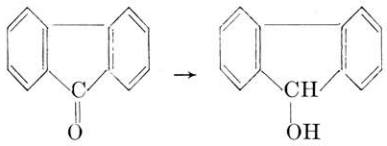
(2) Hydrogenation of chalcone, (I), to 1,3-diphenylpropanol, (III).

There is no slowing down in hydrogenation after the first stage, (I) → (II), has been passed, especially if the nickel catalyst is slightly alkaline. Actually, it is generally found that alkali greatly accelerates reduction of ketones to carbinols (*10*).

Nickel–ethanol (20 ml. of suspension, containing 4 g. nickel), rendered slightly alkaline with aqueous potassium hydroxide solution, was saturated with hydrogen: chalcone (8.32 g.; 0.04 g. mol) in ethanol (20 ml.) was added and hydrogenated. After 45 minutes absorption ceased; (1545 ml.; theory requires 1792 ml.). The ethanol filtrate was concentrated, felted crystals which separated were removed, and the filtrate fractionally distilled. 1,3-Diphenylpropanol, a colorless oil, boiling sharply at 195° under 7 mm. pressure, distilled over with unusual rapidity (6 g.; yield 77 per cent).

Derivatives. The *p*-nitrobenzoyl derivative of 1,3-diphenylpropanol was prepared by heating the alcohol (0.5 g.) with slight excess (0.5 g.) of *p*-nitrobenzoyl chloride (crystallized from petroleum, b. p. 80–100°) in pyridine (1 ml.) by immersing in boiling water for one hour, treating the mixture with water, then with 5 per cent sodium hydroxide solution. The residue crystallized from petroleum (60–80°) in feathery crystals, m. p. 89–90° (found: C, 73.2; H, 5.5; N, 4.0. Calculated for $C_{22}H_{19}O_4N$, C, 73.1; H, 5.3; N, 3.9 per cent) as found by Pfeiffer, *et al.* (*11*).

(*D*) *Reduction of Fluorenone to Fluorenol.*



Fluorenone (0.9 g.) was hydrogenated in presence of nickel–ethanol (1 g. nickel/40 ml. ethanol) and 10 per cent potassium hydroxide solution (1 ml.). Reduction to fluorenol, m. p. 152°, took 5 minutes (0.73 g. yield 80 per cent). Hydrogenation at room temperature, in absence of alkali, is incomplete even after 55 minutes. For further information regarding this hydrogenation, and that of fluorenone-1-carboxylic acid, see Forrest and Tucker (*12*).

Benzophenone has been hydrogenated by Adkins and Billica (*3d*) in presence of triethylamine and W-6 Raney nickel (the most active form) to benzhydrol. Here, as in other hydrogenations of the keto group, addition of a base accelerated the reaction (*10*).

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