Organic Syntheses

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Working with Hazardous Chemicals

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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Organic Syntheses, Coll. Vol. 3, p.176 (1955); Vol. 29, p.24 (1949).

CATALYST, RANEY NICKEL, W-6

[With high contents of aluminum and adsorbed hydrogen]

$$NiAl_2 \;+\; 6\;\; NaOH \;\xrightarrow{H_2O\;\; RaneyNickelW\text{-}6}\; + \;\; 2\;\; Na_3AlO_3 \;+\; 3\;\; H_2$$

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1. Procedure

> *Caution! The Raney nickel catalysts described below cannot be used safely under all conditions of temperature, pressure, and ratio of catalyst to hydrogen acceptor which are employed with less active nickel catalysts. They are particularly effective for low-pressure hydrogenations. No difficulty has been encountered in their use of temperatures below 100°, or above 100° if the ratio of catalyst to possible hydrogen acceptor is 5% or less. Outside these limits their use sometimes has led to reactions proceeding with violence. In one case a hydrogenation proceeding at 125° and 5000 lb. showed a pressure rise to considerably more than 10,000 lb. before the reaction could be stopped or the pressure released. Several instances of sudden increases in pressure have been noted when 10–15 g. of catalyst was used with a similar amount of hydrogen acceptor in 100 ml. of ethanol in the temperature range of 100–150° under 5000 lb. of hydrogen in a bomb of 270 ml. void. Accordingly the catalysts should be used with caution for high-pressure hydrogenations.*

W-6 *Raney nickel catalyst*. In a 2-l. Erlenmeyer flask equipped with a thermometer and a stainless-steel stirrer are placed 600 ml. of distilled water and 160 g. of c.p. sodium hydroxide pellets. The solution is stirred rapidly and allowed to cool to 50° in an ice bath equipped with an overflow siphon. Then 125 g. of Raney nickel-aluminum alloy powder is added in small portions during a period of 25–30 minutes. The temperature is maintained at 50 ± 2° by controlling the rate of addition of the alloy to the sodium hydroxide solution and the addition of ice to the cooling bath. When all the alloy has been added, the suspension is digested at 50 ± 2° for 50 minutes with gentle stirring. It is usually necessary to remove the ice bath and replace it with a hot-water bath to keep the temperature constant. After this period of digestion the catalyst is washed with three 1-l. portions of distilled water by decantation (Note 1).

A glass test tube approximately 5.1 cm. in diameter and 38 cm. in length with a side arm sealed 6 cm. from the top is used as the container for washing the catalyst. The tube is closed with a rubber stopper clamped or wired in place tightly enough to withstand a gas pressure of 0.5 atm. The stopper contains three holes through which extend: (1) a tube 10 mm. in diameter reaching to the bottom of the test tube, for admitting distilled water; (2) a T-tube for equalizing gas pressures; (3) a gas-tight bushing through which the ¼-in. shaft of a stainless-steel stirrer projects to the bottom of the washing tube. A 5-l. aspirator bottle containing distilled water is so placed that water will flow from it through a stopcock to the. bottom of the washing tube. The side arm of the test tube is connected by pressure tubing to a 5-l. aspirator bottle that serves as an overflow from which the water may be allowed to flow through a stopcock to a drain. A source of distilled water is connected to the reservoir. Other connections and the general arrangement of the apparatus are shown in Fig. 8, and details of the construction of the gas-tight brass bushing are given in Fig. 9. Rubber pressure tubing and stoppers used in making the connections should be boiled with 5% sodium hydroxide and rinsed with water to remove sulfur. All connections should be wired in place to withstand a pressure of 0.5 atm. (7.5 lb.).

Fig. 8. Apparatus for washing catalyst. It is convenient to have the inlet tube for wash water sealed into the bottom of the chamber rather than introduced through the stopper as shown.

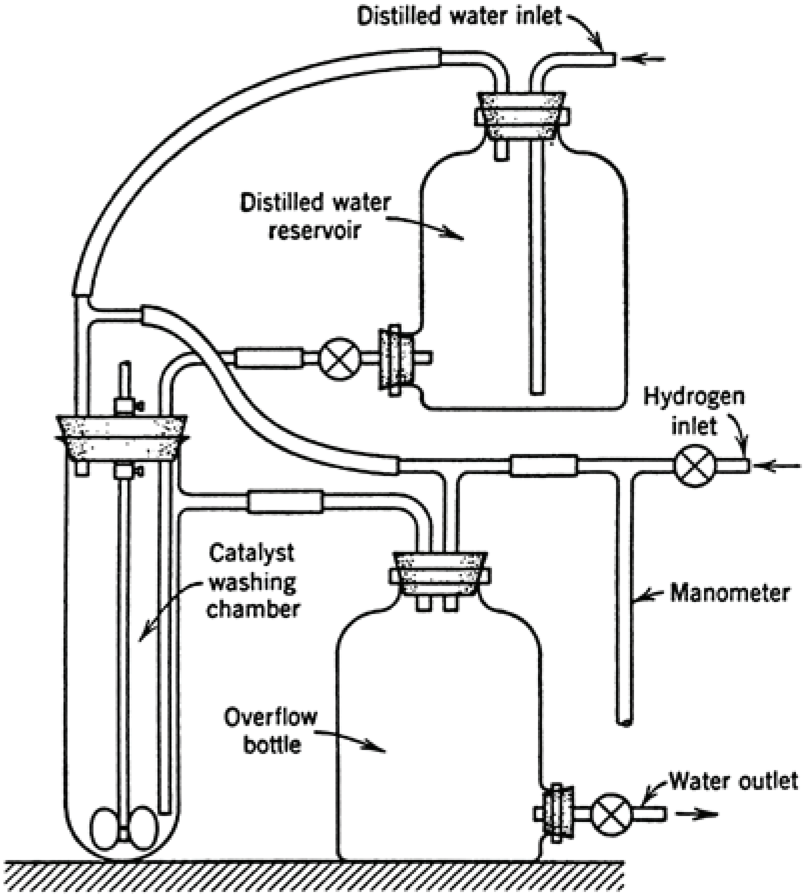
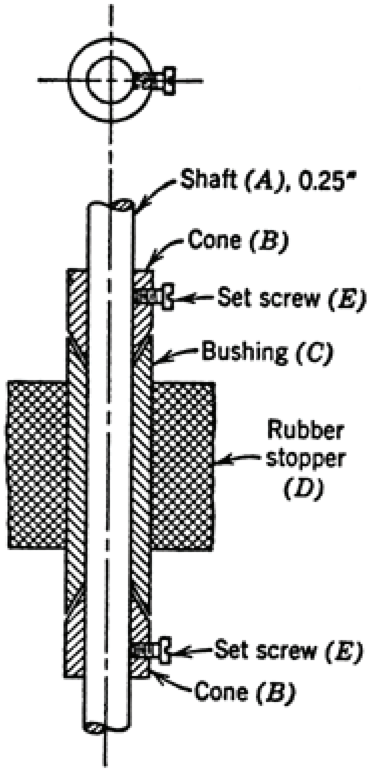


Fig. 9. Gas-tight brass bushing. The gas-tight bushing for the shaft of the stirrer consists of three parts: two cones (*B*) which fit the shaft snugly and are attached to it by set screws (*E*); and a bushing (*C*) so cut that the cones fit into it at top and bottom. The two cones are placed on shaft *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 by 65 mm., and it is held in a rubber stopper (*D*).



The catalyst sludge is transferred to the washing tube immediately after its third washing by decantation. The last portions are rinsed from the flask into the washing tube with distilled water, and the tube, reservoir, and overflow bottle are nearly filled with distilled water. The apparatus is assembled rapidly, and hydrogen is introduced through the inlet while most of the water in the overflow bottle is displaced through the outlet. The outlet then is closed, and hydrogen is admitted until 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 opened simultaneously 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 l. of water has passed through the catalyst, the stirrer and the flow of water are stopped, the pressure is 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. portions of 95% ethanol, each addition being followed by centrifuging. 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 kept in a closed bottle filled with absolute ethanol and should be stored at once in a refrigerator. The total elapsed time from the beginning of the addition of the alloy to the completion of the preparation should be not more than about 3 hours (Note 2), (Note 3), and (Note 4).

2. Notes

1. 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% ethanol. It is then washed three times by stirring, not shaking, with 150-ml. portions of 95% ethanol, with centrifuging after each addition. In the same manner, the catalyst is washed three times with absolute ethanol and is at once stored in a refrigerator in a closed bottle filled with absolute ethanol. The catalyst so prepared contains alkali. This may be advantageous for various reasons in the hydrogenation of ketones, phenols, and nitriles. In

certain cases the alkali may have a harmful effect upon a hydrogenation.

2. The volume of the settled catalyst (W-6) in ethanol is about 75–80 ml. containing about 62 g. of nickel and 7–8 g. of aluminum. The catalyst is extremely pyrophoric when exposed to the air in a dry condition, and it should be kept wet with solvent at all times. It amounts to about 28 "half teaspoonfuls" if it is so measured. The catalyst loses some of its special activity upon standing but seems to be quite active for about 2 weeks when stored in a refrigerator. After this period it is similar in activity to the Raney nickel made by an earlier procedure.[1] The W-3 to W-7 catalysts all lose their special activity rather rapidly when stored under water.

3. A somewhat less active but nevertheless excellent catalyst, referred to as W-5, is made by the procedure described above 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.[2]

4. Raney nickel prepared by the procedure described for W-6 will bring about the hydrogenation of alkyne and alkene linkages, of aldehydes, ketones, oximes, nitriles, nitro compounds, and benzenoid and pyridinoid nuclei under the conditions of temperature and pressure normally employed with platinum and palladium catalysts.[3] At higher pressures W-6 Raney nickel brings about reactions at a more rapid rate and at lower temperatures than Raney nickel prepared by the older procedures.

3. Discussion

The various procedures for the preparation of Raney nickel[4] from the nickel-aluminum alloy differ from one another in the method of adding the alloy, in the concentration of sodium hydroxide, in the temperature and duration of digestion, and in the method of washing the catalyst free of sodium aluminate and alkali. For convenience in reference, the Raney nickel catalysts prepared by various procedures have been designated W-1,[5] W-2,[1] W-3,[2,6] W-4,[2,6] W-5,[3] W-6,[3] and W-7.[3] They have been compared as to activity against β-naphthol.[7] A Raney nickel catalyst is available commercially from the Gilman Paint and Varnish Company, Chattanooga, Tennessee.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 181
- Org. Syn. Coll. Vol. 3, 358
- Org. Syn. Coll. Vol. 4, 603
- Org. Syn. Coll. Vol. 5, 102

References and Notes

1. *Org. Syntheses*, **21**, 15 (1941).
2. Pavlic and Adkins, *J. Am. Chem. Soc.*, **68**, 1471 (1946).
3. Adkins and Billica, *J. Am. Chem. Soc.*, **70**, 695 (1948).
4. Murray Raney, U. S. pat. 1,628,190 [*C. A.*, **21**, 2116 (1927)].
5. Covert and Adkins, *J. Am. Chem. Soc.*, **54**, 4116 (1932).
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7. Adkins and Krsek, *J. Am. Chem. Soc.*, **70**, 412 (1948).

Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

W-6 Raney nickel

Raney nickel-aluminum alloy powder

W-7 Raney nickel

W-4 Raney nickel

ethanol (64-17-5)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

β-naphthol (135-19-3)

sulfur (7704-34-9)

aluminum (7429-90-5)

platinum (7440-06-4)

nickel,
Raney nickel (7440-02-0)

palladium (7440-05-3)

nickel-aluminum

sodium aluminate (1302-42-7)