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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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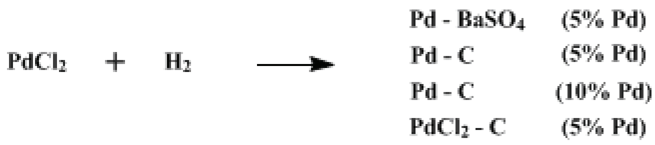
PALLADIUM CATALYSTS

$$Na_2PdCl_4 + CH_2O + NaOH \longrightarrow Pd + HCOONa$$



$$PdCl_2 + H_2 \longrightarrow \begin{array}{ll} Pd\text{-}BaSO_4 & (5\%\ Pd) \\ Pd\text{-}C & (5\%\ Pd) \\ Pd\text{-}C & (10\%\ Pd) \\ PdCl_2\text{-}C & (5\%\ Pd) \end{array}$$

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1. Procedure

(Note 1)

A. *Palladium on barium sulfate catalyst* (5% *Pd*). A solution (Note 2) of 8.2 g. of palladium chloride (0.046 mole) in 20 ml. (0.24 mole) of concentrated hydrochloric acid and 50 ml. of water is prepared. To a rapidly stirred, hot (80°) solution of 126.2 g. (0.4 mole) of reagent barium hydroxide octahydrate in 1.2 l. of distilled water contained in a 4-l. beaker (Note 3) and (Note 4) is added all at once 120 ml. (0.36 mole) of 6 *N* sulfuric acid. More 6 *N* sulfuric acid is added to make the suspension just acid to litmus (Note 5). To this hot barium sulfate suspension (Note 6) are added the palladium solution and 8 ml. (0.1 mole) of 37% formaldehyde solution. The suspension is then made slightly alkaline to litmus with 30% sodium hydroxide solution, constant stirring being maintained. The suspension is stirred 5 minutes longer, and then the catalyst is allowed to settle (Note 7). The clear supernatant liquid is decanted and replaced by water, and the catalyst is resuspended. The catalyst is washed by decantation eight to ten times. After the final decantation, the catalyst is collected on a 90-mm. medium-porosity sintered-glass funnel (Note 8). Most of the water is removed from the cake, but not enough to cause the cake to break or channel. The filter cake is washed with 250 ml. of water in five portions, the last being removed as completely as possible by filtration. The funnel and its contents are then placed in an oven at 80° until the catalyst is dry. The catalyst (93–98 g.) is powdered and stored in a tightly closed bottle (Note 9).

B. *Palladium on carbon catalyst* (5% *Pd*). A suspension of 93 g. of nitric acid-washed Darco G-60 (Note 10) in 1.2 l. of water contained in a 4-l. beaker (Note 3) and (Note 4) is heated to 80°. To this is added a solution of 8.2 g. (0.046 mole) of palladium chloride in 20 ml. (0.24 mole) of concentrated hydrochloric acid and 50 ml. of water (Note 2). Eight milliliters (0.1 mole) of 37% formaldehyde solution is added. The suspension is made slightly alkaline to litmus with 30% sodium hydroxide solution, constant stirring being maintained. The suspension is stirred 5 minutes longer. The catalyst is collected on a filter and washed ten times with 250-ml. portions of water. After removal of as much water as possible by filtration, the filter cake is dried (Note 11), first in air at room temperature, and then over potassium hydroxide in a desiccator. The dry catalyst (93–98 g.) is stored in a tightly closed bottle.

C. *Palladium chloride on carbon* (5% *Pd*). A solution of 8.2 g. (0.046 mole) of palladium chloride in 20 ml. (0.24 mole) of concentrated hydrochloric acid and 50 ml. of water is prepared (Note 2). The solution is diluted with 140 ml. of water and poured over 92 g. of nitric acid-washed Darco G-60 (Note 10) in an 8-in. evaporating dish (Note 3). After the palladium chloride solution has been thoroughly mixed with the carbon, the whole mixture is dried, first on a steam bath and then in an oven at 100°, with occasional mixing until completely dry. The mass (98–100 g.) is powdered and stored in a closed bottle.

The required quantity of palladium chloride on carbon is transferred to a hydrogenation bottle and reduced with hydrogen in the solvent to be used for the hydrogenation (Note 12) and (Note 13). When no more hydrogen is absorbed by the catalyst, it is collected (Note 14) on a sintered-glass funnel and washed with more of the solvent to remove the hydrogen chloride, and then returned to the reduction bottle, the last being washed in with the solvent. The material to be hydrogenated is then added and the hydrogenation is completed in the usual way.

D. *Palladium on carbon catalyst* (10% *Pd*). A solution of 8.33 g. of palladium chloride in 5.5 ml. of concentrated hydrochloric acid and 40 ml. of water is prepared by heating the mixture on a steam bath (Note 2) and (Note 15). The resulting solution is poured into a solution of 135 g. of sodium acetate trihydrate in 500 ml. of water contained in a 1-l. reduction bottle (Note 16). Forty-five grams of Norit (Note 10) is added, and the mixture is hydrogenated until absorption ceases after 1–2 hours. The catalyst is collected on a Büchner funnel and washed with 2 l. of water in five portions. The filter cake, after removal of most of the water, is dried in air and then in a desiccator over calcium chloride (Note 11). The catalyst (48–50 g.) is stored, after being powdered, in a tightly closed bottle.

2. Notes

1. The four procedures given for the preparation of palladium catalysts differ in that in A the support is barium sulfate or barium carbonate whereas in the others the support is carbon. In procedures A and B, alkaline formaldehyde is the reducing agent; in C and D, hydrogen is used. The catalysts A, B, and D are prepared and stored until required with the palladium in the reduced form ready for use. In C,[1] the palladium salt is reduced to the metal as needed, so that there is no loss of activity during storage. Catalyst A is similar to that usually recommended for Rosenmund reductions; D is essentially that developed by Hartung[2] and extensively used by Cope[3] and others. Catalyst D carries twice as much palladium per unit weight as the others.
Catalysts reduced with formaldehyde carry no adsorbed hydrogen and are less pyrophoric. Barium carbonate as a support may sometimes be advantageous in that the neutrality of the hydrogenation mixture may be maintained. Barium sulfate or barium carbonate may be a better support than carbon, which may, in some instances, so strongly adsorb the derived product that recovery is difficult or incomplete. Palladium may be more completely and easily recovered from a spent catalyst where carbon rather than barium sulfate is the support. In general, the submitter prefers a catalyst prepared according to procedure C.
2. Since palladium chloride dissolves rather slowly in aqueous acid, the mixture is heated on a steam bath for about 2 hours, or until solution is complete. If the dihydrate of palladium chloride is used the quantity should be increased to 9.9–10.0 g.
3. The entire preparation is carried out with all-glass or porcelain equipment in order to prevent contamination with iron or other metals.
4. The catalyst may be prepared in ten times the amount given here, with a 20-l. battery jar in place of the beaker.
5. The rapid addition of sulfuric acid is made to give finely divided barium sulfate.
6. An equal weight of precipitated barium carbonate (93 g.) may be substituted for the barium hydroxide and sulfuric acid to give a palladium on barium carbonate catalyst. The amount of hydrochloric acid should then be reduced to 8.2 ml.
7. After 5 minutes, the solution is colorless and free of palladium chloride.
8. A Büchner funnel may be used, but filtration through paper is very slow. The washing process may be carried out by centrifugation instead of filtration.
9. The palladium may be conveniently separated from the barium sulfate by solution in aqua regia. The used catalyst is collected from the reaction mixture on a sintered-glass funnel. The organic material is removed with suitable solvents, and the solvents are replaced by water. The palladium is dissolved in aqua regia and is washed out with dilute hydrochloric acid, the solutions being collected for recovery of the metal. For recovery of the palladium from carbon, the mass is ignited and the ash is extracted with aqua regia for several hours. The palladium solution is filtered, and any residue is reignited and then treated with alkaline formaldehyde solution to reduce any oxides of palladium which may have been formed, and which are only slowly soluble in aqua regia. The solids are collected on a filter, and the palladium is extracted with aqua regia.
10. Norit, Darco, or other carbons may be used. The carbon is heated on a steam bath with 10% nitric acid for 2–3 hours, washed free of acid with water, and dried at 100–110° before use.
11. The palladium on carbon catalysts should be dried at room temperature or the carbon may ignite.

These catalysts are first dried in air and then over potassium hydroxide (or calcium chloride) in a desiccator.

12. The solvent is conveniently that in which the hydrogenation is to be done. During the reduction of the palladium chloride, a neutral solvent is to be preferred; any acid or alkali needed for the hydrogenation is added after reduction of the catalyst.

13. The presence of hydrogen chloride during the hydrogenation of many organic compounds is desirable or without effect, so that the washing operations may be omitted in such cases. Thus, the palladium chloride on carbon may be used in the same manner as the prereduced catalysts, i.e., simply added before reduction to the solvent and the hydrogen acceptor.

14. The catalyst should be kept wet with the solvent during the washing process, as it is pyrophoric.

15. The resulting solution is approximately equivalent to 50 ml. of the commercial palladium chloride solution (p. 385) suggested by Hartung and Cope.[3]

16. The checkers reduced the palladium chloride, in three batches, in a 500-ml. bottle. The bottle was not shaken, but the contents were rapidly stirred under a pressure of 1.1 atmospheres of hydrogen. The reduction of each batch required about 5 hours.

3. Discussion

Palladium catalysts have been prepared by fusion of palladium chloride in sodium nitrate to give palladium oxide;[4,5] by reduction of palladium salts by alkaline formaldehyde[6,7,8] or sodium formate,[9] by hydrazine,[10] and by the reduction of palladium salts with hydrogen.[11] The metal has been prepared in the form of palladium black,[6,9] and in colloidal form in water containing a protective material,[10] as well as upon supports. The supports commonly used are asbestos[12] barium carbonate,[13] barium sulfate,[1,7,8,14] calcium carbonate,[15] carbon,[1,11,14,16] kieselguhr,[14,16] silica-gel,[17] and strontium carbonate.[18] The catalysts described here are prepared by modifications of the methods of Schmidt,[8] Rosenmund and Langer,[14] Mannich and Thiele,[11] and Hartung.[2,3]

Polyvinyl alcohol[19] and aluminum oxide[20] have been used as supports for palladium catalysts.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 385
- Org. Syn. Coll. Vol. 3, 626
- Org. Syn. Coll. Vol. 4, 408
- Org. Syn. Coll. Vol. 4, 536
- Org. Syn. Coll. Vol. 4, 887
- Org. Syn. Coll. Vol. 5, 989

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

palladium black

dihydrate of palladium chloride

oxides of palladium

Polyvinyl alcohol

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrogen chloride,
hydrochloric acid (7647-01-0)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

formaldehyde (50-00-0)

iron (7439-89-6)

nitric acid (7697-37-2)

calcium carbonate (471-34-1)

barium sulfate (7727-43-7)

carbon,
Norit (7782-42-5)

potassium hydroxide (1310-58-3)

palladium (7440-05-3)

barium hydroxide (17194-00-2)

barium carbonate (513-77-9)

barium hydroxide octahydrate (12230-71-6)

hydrazine (302-01-2)

sodium formate

sodium nitrate

palladium oxide

palladium chloride (7647-10-1)

aluminum oxide (1344-28-1)

sodium acetate trihydrate (6131-90-4)

strontium carbonate (1633-05-2)