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NOBLE METAL HYDROXIDES ON CARBON NONPYROPHORIC DRY CATALYSTS

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During the past ten years we have had a need for catalysts that are not only dry but also nonpyrophoric prior to coming in contact with hydrogen. The preparation of three such catalysts are described below.

1. PROCEDURE

$Pd(OH)_2$ (20% Pd) on Carbon

$PdCl_2$ (100 g.) (Note 1), carbon, (Darco G-60) (240 g.) and deionized water (2 l.) are mixed and rapidly stirred while being heated to 80° C. $LiOH \cdot H_2O$ (50 g.) (Note 2) dissolved in water (200 ml.) is added all at once and the heating is stopped. The mixture is stirred overnight, filtered, washed with 0.5 v/v% aqueous acetic acid (2 l.). The cake is sucked as dry as possible and dried *in vacuo* at 60° C. Yield 300-320 g. (Note 3). When 1 g. of this catalyst is hydrogenated, it consumes 0.0022-0.0026 moles (Note 4) of hydrogen per gram.

$Rh(OH)_3$ (10% Rh) + $Pd(OH)_2$ (0.1% Pd) on Carbon (Note 5)

$RhCl_3 \cdot 3H_2O$ (52.6 g.) (Note 1), $PdCl_2$ (0.34 g.), carbon (Darco G-60) (180 g.) and water (2 l.) are mixed, rapidly stirred and heated to 80° C. $LiOH \cdot H_2O$ (27 g.) (Note 2) dissolved in H_2O (100 ml.) is added all at once and the heating stopped. The mixture is stirred overnight, filtered and washed with 0.5 v/v% aqueous acetic acid (1 l.). The product is dried *in vacuo* at 65° C. Yield 206-210 g. (Note 3). One gram of this catalyst consumes 0.0022-0.0028 moles (Note 4) of hydrogen in aqueous suspension.

$Ru(OH)_3$ (10% Ru) + $Pd(OH)_2$ (0.1% Pd) on Carbon (Note 5)

$RuCl_3 \cdot 3H_2O$ (52.4 g.) (Note 1), $PdCl_2$ (0.34 g.), carbon (Darco G-60) (180 g.) and water (2 l.) are mixed, rapidly stirred and heated to 80° C. $LiOH \cdot H_2O$ (27 g.) (Note 2) dissolved in water (100 ml.) is added all at once and the heating stopped. The mixture is stirred overnight, filtered and washed with a liter of 0.5 v/v% aqueous acetic acid. The product is dried in vacuo at 65° C. Yield 202-211 g. (Note 3). One gram of catalyst suspended in water consumes 0.0024-0.0025 moles (Note 4) of hydrogen.

2. NOTES

1) All chlorides were obtained from Engelhard Industries, Inc., Newark, New Jersey.

2) The lithium hydroxide monohydrate used was reagent grade.

3) The range in yield results from the difficulty of removing all of the solvent even after drying for 48 hrs. in vacuo at 65° C.

4) The discrepancy between the theoretical uptake of hydrogen and the actual uptake is reconcilable by the fact that Darco G-60 contains reducible matter

5) The palladium hydroxide is incorporated with the rhodium and ruthenium hydroxide in order to shorten the reduction time of these catalysts.

6) Always wet a catalyst with solvent before using.

The foregoing preparations give rise to nonpyrophoric dry catalysts that may be wet with organic solvents without any special precautions. The catalyst that results from the reduction of the metal hydroxide with hydrogen is extremely active.

Palladium catalyst prepared in this manner has been used to debenzylate amines and esters in methanol solution with hydrogen at 3 atmospheres and room temperature. Arylalkyl ketones in acetic acid have been reduced to the hydrocarbon, *e.g.*, acetophenone to ethyl benzene. Aromatic halogen, *i.e.*, chlorine and/or bromine, has been hydrogenolized in 95% ethanol using a base even when attached to a thiophene ring. The unsubstituted ring of naphthalene compounds has been reduced with this catalyst using acetic acid as solvent. Aliphatic nitro compounds have been reduced to amines and hydroxylamines.

Rhodium catalyst made in this manner has been used to saturate a wide variety of aromatic and hetero compounds. At 50 p.s.i., all the pyridine monocarboxylic acids have been hydrogenated in water to the piperidine carboxylic acids. *p*-Aminobenzoic acid has been similarly reduced. Benzoylpyridines have been reduced to hydroxyphenylpiperidines using methanol as solvent with 1 mole of sulfuric acid per mole of compound.

Ruthenium catalyst prepared in this manner has been used to hydrogenate aliphatic ketones or aldehydes to the corresponding carbinols at 50 p.s.i. using MeOH or 95% EtOH as solvent. At higher pressures (1500 p.s.i.) and temperature (100° C) aromatic rings have been reduced. Arylalkyl ketones, *e.g.*, acetophenone, have been hydrogenated to the corresponding cyclohexylalkyl carbinols. Pyridine and napthalene compounds have been completely saturated.