Procedure for the Preparation of the New Nickel Catalyst

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(Received August 19, 1954)

In a preliminary note[1] one of the authors (Y.U.) reported that metallic nickel and copper precipitated from the aqueous solutions of their soluble salts by means of zinc dust are active catalysts for hydrogenation in the presence of caustic alkali or when digested with aqueous caustic alkali before use. Since then, the activity of the new nickel catalyst has been much improved. The following is the procedure for obtaining the greatest activity that has been so far attained.

Ten grams of zinc dust, as fine as possible, and about 3 cc. of distilled water are put in a round flask of 100 cc. capacity and heated on a boiling waterbath. A stirrer reaching the bottom is installed. Ten cc. of an aqueous solution containing 4.04 g. of nickel chloride, $NiCl_2 \cdot 6H_2O$, is heated to ebullition, and added to the zinc dust by means of a pipet, with vigorous agitation in a few sec. The solids are at once collected on a glass filter by suction, washed with a small quantity of hot distilled water, transferred into 160 cc. of 10% aqueous caustic soda contained in an Erlenmeyer flask as quickly as possible, and digested at 50–60° for 15–20 minutes with occasional stirring. Then, the supernatant liquid is removed, and the solids are washed with 40 cc. of distilled water of 50–60° two times, and finally with the solvent of hydrogenation, e. g. ethanol. The rinsings are always removed by decantation.

In this way, a catalyst consisting of about 1 g. of nickel and 4.7 g. of zinc, and acting as good as 1 g. of Raney nickel catalyst (e. g. W 7) is obtained and can be used for hydrogenation or reduction of ketones, nitriles, oximes, a double bond conjugated with a carbonyl or a carboxyl group, etc., at the ordinary temperature and pressure.

Free carboxylic acids diminish the activity of the nickel catalyst. Hence, they are neutralized with caustic alkali before introducing the catalyst, or hydrogenated in solution in aqueous alkali. For instance, cinnamic acid is easily reduced to hydrocinnamic acid in solution in aqueous caustic soda.

In case the alkali remaining on the catalyst is undesirable, digestion in a saturated aqueous solution of sodium chloride followed by washing with hot distilled water will remove the majority of the adsorbed alkali. For instance, the reduction of nitrobenzene to aniline is better performed with a so-treated catalyst.

If 80 cc. instead of 160 cc. of 10% caustic soda is used in digestion, the activity is increased by about 10%, but the weight of the catalyst amounts to about 10 g. corresponding to the more quantity of matters remaining undissolved.

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[1] Y. Urushibara, This Bulletin, **25**, 280 (1952).