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Preparation of a Raney Nickel Catalyst

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Mozingo summarized his experiences in the laboratories of the Universities of Wisconsin and Illinois in the preferred procedure for preparing Raney nickel catalyst of high and consistent activity.[1] This procedure was a development of one earlier described which was based on private communications and the patent of Murray Raney.[2,3]

Incidental to a study in 1941 of the hydrogenation of esters,[4] a more active catalyst than that resulting from the directions outlined by Mozingo has been prepared by lowering the temperature and shortening the period of reaction of the alloy with the alkaline solution, and by a more effective method for washing the catalyst out of contact with air. The time elapsing from the beginning of the preparation until the completion of the digestion period is reduced from twelve hours or more to less than one and one-half hours, the temperature never being allowed to go above 50° at any stage of the process.

The usefulness of the more active Raney nickel catalyst makes it seem worthwhile to describe now the procedure of its preparation. The catalyst as described is active for the hydrogenation of esters to alcohols at 25 to 50°, and in various other hydrogenations at lower temperatures than are feasible with other nickel catalysts. In a recent publication, Wilds and Beck[5] have described experiments in which the catalyst prepared by the procedure given herewith brought about the partial hydrogenation of the naphthalene nucleus at room temperatures and atmospheric pressure.

The procedure for the preparation of the catalyst is as follows:

In a two-liter Erlenmeyer flask equipped with thermometer and stainless steel Hershberg-type stirrer is placed 128 g. of sodium hydroxide in 500 ml. of water. The flask is immersed in a bath of cold running water and when the heat of solution has subsided to 50°, 100 g. of Raney nickel-aluminum alloy is added in small (2–4 g.) portions to the very rapidly stirred solution over a period of twenty-five to thirty minutes. By controlling the rate of addition of the alloy, the temperature is maintained at 50 ± 2°; sudden rushes of foam, which threaten to carry over the lip of the flask are collapsed by the addition of a few drops of ethanol. When all the alloy has been added, the cooling bath is removed and the curdy suspension is digested at 50° for fifty minutes with gentle stirring; the heat of solution of the remaining aluminum is usually sufficient to balance the radiation losses although slight warming or additional cooling may be required to maintain the digestion temperature. Following this, the catalyst is washed in the reaction flask several times by decantation with distilled water and then transferred to a 500-ml. graduated cylinder.

The graduated cylinder containing the wet catalyst is fitted with a stainless steel stirrer with a 2 × 3 cm. paddle of the same material. Distilled water is admitted into the bottom of the cylinder by means of a long, off-set 8-mm. glass tube connected, by means of a 2-hole rubber stopper, to an inverted 5-liter round bottom flask suspended above, and to one side of the washing chamber. The second hole of the rubber stopper is fitted with a straight length of 8 mm. glass tubing extending to the top of the inverted flask. The flow of wash water into the cylinder is controlled by the rate with which air is admitted into the reservoir; this is conveniently accomplished by fitting a capillary leak or a pinch clamp-rubber tubing arrangement to the straight tube in the rubber stopper. The overflow from the cylinder is drawn off with an aspirator through a safety bottle, a 500-ml. suction flask is sufficient for this purpose.

By proper choice of motor speed, the catalyst is suspended evenly to a depth of 20 cm. or 0.75 of the length of the water column in the cylinder. If the digestion has been incomplete, some of the Raney nickel, because of its high aluminum content and, therefore, low density, may be carried over with the wash water; however, this may be recovered from the safety bottle. Proper digestion will yield a thick curdy suspension which will exhibit no tendency to disintegrate and rise above the normal suspension depth.

After about 15 liters of water has been flushed through the catalyst (two to three hours) or until the wash water tests neutral to litmus, the catalyst is allowed to settle and the water column decanted. The heavy sludge is transferred to a 250-ml. centrifuge bottle, and washed three times by stirring, not shaking, with 150 ml. of 95% ethyl alcohol, centrifuging after each addition. In the same manner the catalyst is washed three times with absolute alcohol; during these latter washings, if the catalyst has been prepared and washed properly, the nickel will lose its former fluffiness and become almost colloidally dispersed in the alcohol. The catalyst is stored under alcohol or other liquid out of contact with air as is necessary in the case of all Raney catalysts.

Summary

A procedure for preparing Raney nickel from the nickel aluminum alloy is described. The catalyst so obtained is more active, particularly at temperatures below 100° than is Raney nickel prepared by other procedures known to the authors.

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[1] Mozingo, "Organic Syntheses," **21**, 15 (1941).

[2] Covert and Adkins, THIS JOURNAL, **54**, 416 (1932).

[3] Murray Raney, U. S. Patent No. 1,628,190 (1927).

[4] Christman and Levene, *J. Biol. Chem.*, **124**, 453 (1938).

[5] Wilds and Beck, THIS JOURNAL, **66**, 1688 (1944).