A New Type of Urushibara Nickel Catalyst

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(Received June 24, 1958)

The preparation[1], the application[2] and the characteristics[3] of Urushibara nickel catalyst, prepared from nickel chloride and zinc dust, have already been reported. In this paper the procedure of preparing a new nickel catalyst, prepared from nickel chloride and aluminum grains in place of zinc dust and named Urushibara nickel BA or U-Ni-BA in abbreviation, is presented. Aluminum grains of a proper size must be used to obtain an active catalyst. Commercially available aluminum powder proved to be invalid. Using aluminum grains of 40~80 meshes, a new type of Urushibara nickel was prepared: the precipitated nickel from aqueous nickel chloride solution with such aluminum grains was digested with aqueous caustic alkali, and a new hydrogenating catalyst was obtained. This nickel catalyst proved to be very effective for hydrogenation of various organic compounds. Above all, benzene, aniline and methyl salicylate were respectively hydrogenated under a high pressure to cyclohexane, cyclohexylamine and methyl hexahydrosalicylate, these hydrogenation being unsuccessful with Urushibara nickel B or A.

A procedure for the preparation of the most active catalyst was determined from the results of hydrogenation of acetone under ordinary pressure.

Aluminum grains of 40~80 meshes (10 g.) are washed with water and treated with 50 ml. of 3% sodium hydroxide solution until the mixture becomes hot and vigorously frothy. To this mixture is added water to suppress the frothing and the upper liquor is decanted. The aluminum grains are washed well with water to remove a trace of alkali. They are transferred into a 500 ml. wide-mouthed, round-bottomed flask or beaker and warmed with a little water on a boiling water bath. To this is added 20 ml. of hot aqueous nickel chloride solution which contains 2 g. of nickel. Occasional stirring is continued until the slushy reaction mixture becomes nearly solid. The solids are crushed two or three times with hot water to remove water-soluble products. To a mixture of the solids and a little water is cautiously added with stirring 250 g. of 20% sodium hydroxide solution in several portions. As a addition of the first portion is followed by a violent reaction, good stirring and cooling with ice are necessary to prevent the contents running over. After a half

1) Y. Urushibara, This Bulletin, **25**, 280 (1952); Y. Urushibara et al., ibid., **27**, 480 (1954); Y. Urushibara et al., ibid., **28**, 446 (1955).

2) S. Nishimura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 340 (1956); ibid., **78**, 1741 (1957); ibid., **79**, 56 (1958); K. Hata et al., ibid., **77**, 1405 (1956); ibid., **78**, 186 (1957); This Bulletin, **30**, 431 (1957).

3) Y. Urushibara et al., This Bulletin, **29**, 815 (1956).

part of the alkali is added during about ten minutes, the other half is added at once to the reaction mixture, which is continuously stirred until the generation of hydrogen gas ceases. The temperature of the reaction mixture should be kept below 60°C throughout this operation. After being kept for a few minutes, the upper liquor of the dark reaction mixture is carefully

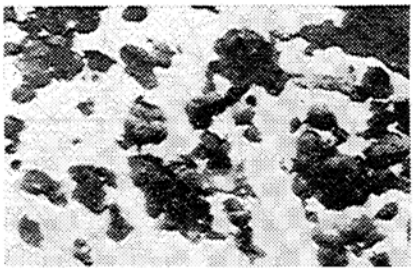

Fig. 1. Micro-photograph of Urushibara nickel BA.

decanted and the residue is washed five times with each 100 ml. of hot water and then thrice with each 50 ml. of ethanol. The solids are transferred into a hydrogenating vessel with the solvent to be used. In these stages contact with air must be avoided as far as possible. Distilled water is used for wash, and every washing is removed by decantation. In this way a very active catalyst containing about 2 g. of nickel, a small amount of aluminum and a trace of alkali is obtained.

A micro-photograph of this catalyst is given. This photograph shows that ion-exchange occurred on the surface of aluminum grains and then inner aluminum was dissolved out by the action of sodium hydroxide solution.

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