A New Preparation of Catalytic Nickel

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The nickel catalyst which is now named Urushibara nickel B or U-Ni-B in abbreviation is prepared by adding aqueous nickel chloride to an excess of zinc dust and digesting the precipitated nickel with aqueous caustic alkali1),2). The activity of the catalyst depends largely on the method of precipitation. A high temperature, a concentrated solution of nickel chloride, and a quick addition of the solution to the zinc dust with vigorous stirring, namely conditions favoring the precipitation of finely divided nickel, produce a high activity. The precipitated nickel shows a high catalytic activity only after being treated with caustic alkali. The nature of the activating effect of caustic alkali, however, has not yet been elucidated.

In this paper another new hydrogenating nickel catalyst, named Urushibara nickel A or U-Ni-A in abbreviation, is announced.

The solids from aqueous nickel chloride and zinc dust, prepared in the same way as in the preparation of U-Ni-B2), are collected on a glass filter, washed with hot distilled water, and treated with acetic acid or propionic acid instead of caustic alkali. For instance, the solids from 4. 04 g. of nickel chloride and 10 g. of zinc dust, after being washed with hot distilled water, are quickly transferred into 160 cc. of 13% acetic acid without heating. When the generation of hydrogen gas subsides, the solids are again collected on a glass filter, washed with distilled water of 50–60° and then with the solvent of hydrogenation, and transferred into the hydrogenating vessel. Contact with air is avoided as far as possible. In this way very active U-Ni-A is obtained.

While the U-Ni-B contains a large proportion of metallic zinc, the U-Ni-A contains only a little, if any, and has a much smaller bulk. The new U-Ni-A acts very well, for instance, in the catalytic reduction of nitrobenzene to aniline and of ethyl cinnamate to ethyl hydrocinnamate. The U-Ni-B is very active in the reduction of ketones and also in the reduction of nitrobenzene if it is washed thoroughly, while the U-Ni-A exhibits excellent activity in the reduction of ketones if a small amount of caustic alkali is added.

The same precipitated nickel acquires a high activity on treatment with either caustic alkali or acetic acid. Thus, it is very probable that the activating effect of these reagents consists in uncovering the inherently active nickel surfaces, but not in creating any active substances or state on the surfaces. The precipitated nickel, as it is precipitated, contains zinc hydroxide and basic zinc chlorides besides excessive metallic zinc. It is concluded from the facts stated below that the basic chlorides must be removed in order to recover the active surfaces.

Caustic alkali quickly removes the basic chlorides from the precipitated nickel, and digestion with an amount of aqueous caustic alkali insufficient to dissolve completely the colloidal hydroxide and metallic zinc gives a quite active catalyst. On the other hand, the far less active solids prepared with an insufficient amount of acetic acid release again chloride ions on further treatment with acetic acid and become highly active3). For obtaining a highly active nickel with acetic acid, such an amount as is sufficient to dissolve nearly completely the metallic zinc and partly even the nickel is necessary. Stronger acids, for instance, formic acid and hydrochloric acid, are not suitable for producing catalytic activity.

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

2) Y. Urushibara, and S. Nishimura, ibid., 27, 480 (1954). For the exact procedure see loc. cit.

3) Added in proof: Basic zinc acetate also diminishes the activity, because the U-Ni-B loses partly its activity on treatment with insufficient acetic acid but regains the original activity when treated with sufficient acetic acid.

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