This invention relates to the reactivation of spent nickel alloy catalysts, and more particularly to the reactivation of spent nickel-aluminum alloy catalysts by treatment with dilute aqueous nitric acid. It has long been known that, in hydrogenation reactions accompanied by the formation of small amounts of hydrogen sulfide, nickel catalysts lose their efficiency after a few weeks of operation. Numerous methods have been proposed for reactivating spent nickel catalysts (Berkman, Morrell and Egloff, “Catalysis,” pages 296 to 299, Reinhold Publishing Corporation, 1940). In a like manner, nickel-alloy catalysts, after protracted periods of use, become relatively inactive. Moreover, methods which have been proposed for the reactivation of ordinary nickel or supported nickel catalysts are found to be entirely unsatisfactory for the reactivation of nickel-aluminum alloy catalysts. For example, reactivation procedures which involve dissolving the nickel and precipitating the same as an insoluble nickel compound, followed by reducing such compound to metallic nickel are, of course, inoperative as methods for producing reactivated nickel-aluminum alloy catalysts. Also, spent nickel-aluminum alloy catalysts are not reactivated by treatment with strong caustic soda.

An object of this invention is to provide a simple, effective, and inexpensive method for reactivating spent nickel-aluminum alloy catalysts. Other objects will appear hereinafter.

These objects are accomplished in accordance with the invention by treating spent nickel-aluminum alloy catalysts with dilute nitric acid, preferably of 8 to 23% concentration, whereby the spent catalyst is converted into a reactivated nickel-aluminum alloy catalyst having an activity which is substantially as great as the activity of the original catalyst. The nickel-aluminum alloy catalysts which are employed in the practice of this invention are prepared in general by treating granules (2 to 4 mesh) of nickel-aluminum alloy with caustic soda, thereby dissolving the surface aluminum and leaving an active surface of nickel over an unchanged alloy core. After this catalyst has been used for a period of weeks in the hydrogenation of organic substances containing minute traces of sulfur compound (as, for example, in the hydrogenation of benzene to cyclohexane), the catalyst becomes deactivated due to the formation of an enamel-like coating, about 0.015 to 0.020 inch thick, covering the surface of each granule. This coating is impervious to caustic soda solution, which precludes the activation of the alloy by the method above described for the initial activation of the surface of the catalyst. While the nature of this enamel-like coating is not fully understood, the evidence seems to indicate that it is a composition comprising nickel sulfide and aluminum oxide.

In the activation of this spent nickel-aluminum alloy catalyst it is preferable to employ nitric acid of 8 to 23% concentration. During the treatment of the catalyst with nitric acid of this concentration a small amount of nickel is unavoidably brought into solution. It is, of course, desirable that such loss of nickel be kept at a minimum. Nitric acid which is not sufficiently dilute has an oxidizing action, and the resulting solution contains nickel sulfate. This oxidizing action is especially undesirable, because nickel sulfate (unlike nickel nitrate) is not readily recovered in the form of catalytically active nickel. If nitric acid of the proper concentration is employed, the sulfur in the coating on the spent catalyst granules is liberated in the form of hydrogen sulfide, which is easily expelled from the nitric acid mixtures.

Generally, according to the invention, the concentration of the nitric acid is so controlled as to give a reasonable rate of removal of coating on the catalyst granule without producing free sulfur, or nickel sulfate in the nitric acid solution. Thus, there is a critical optimum range of nitric acid concentration which gives rise to high quality reactivated nickel-aluminum alloy catalysts while simultaneously producing as a byproduct recoverable nickel which can be obtained readily in catalytically active form. This optimum concentration of nitric acid for the accomplishment of this purpose, according to the invention, is from 15% to 21%. The temperature should be about 80° to 105° C., preferably about 98° to 100° C.

The reactivation of nickel-aluminum alloy catalysts, in accordance with this invention, is preferably conducted in a reaction vessel which is equipped with a means for vigorous mechanical agitation (such as stirring), since the removal of the insoluble coating from the surface of the granules is assisted by abrasion. The invention is illustrated further by means of the following example.

Example.—Into a reaction vessel equipped with a mechanical stirrer is introduced 1669 parts by weight of water and 1000 parts of spent nickel alloy catalyst. The mixture is stirred, and small portions (10 parts each) of 95% nitric acid are added, sufficiently slowly to avoid loss by foaming, until the total added quantity is 350 parts. The
aqueous phase contains nitric acid of about 15% to 19% concentration. As the reaction proceeds, the temperature is maintained at 65° to 100° C. The stirring is continued, and from time to time samples of the catalyst granules are removed and tested by determining whether or not they liberate hydrogen from a 0.1 normal sodium hydroxide solution at 25° C. If the granules do not liberate hydrogen freely, the reactivation process is continued. When it is found that the granules have been satisfactorily reactivated, as determined by these tests, the reaction mixture is cooled down to 60° C, and the liquid portion of the mixture is withdrawn and pumped to a nickel recovery unit, since it contains small amounts of nickel nitrite. The granules remaining in the reaction vessel are then washed with distilled water and are dried at 150° C, for 4 hours. The resulting dry material is screened to 2 to 4 mesh. The fines from this operation are melted to form ingots of alloy which can be crushed and screened to the proper size for reuse.

The nitric acid-nickel nitrate solution, which is withdrawn from the reaction vessel as stated above, is heated to a temperature of 65° C, and sufficient sodium carbonate is added at the rate of 20 parts per minute, to raise the pH to 7.5. After the precipitation is complete the slurry thus obtained is washed 4 times with distilled water (500 parts for each wash). The precipitate is then filtered and dried at 150° C, for 4 hours. A high quality, recovered nickel catalyst is thus obtained. This is set aside to be used for purposes not requiring the use of nickel-aluminum alloy catalysts.

It will be understood that the above example is illustrative only and is not intended to limit the invention in any way. While the catalyst described in the example is preferably of about 2 to 4 mesh grain size it will be appreciated that the method is also applicable to catalysts of larger or smaller grain size.

The reactivated nickel-aluminum alloy catalyst may be employed in the hydrogenation of organic substances generally, and is particularly effective in the hydrogenation of aromatic hydrocarbons to the cycloaliphatic hydrocarbons as in the conversion of benzene to cyclohexane.

Since many different embodiments of the invention may be made without departing from the spirit and scope thereof it is to be understood that we do not limit ourselves except as set forth in the following claims.

I claim:

1. A process for reactivating spent granular nickel-aluminum alloy catalysts, which have become deactivated through prolonged use and formation of a sulfur-containing film thereon, which comprises subjecting the said spent catalysts to the action of dilute aqueous nitric acid having a concentration of about 15% to 21% at a temperature of about 65° to 100° C, continuing the said treatment with the said dilute aqueous nitric acid until the sulfur has been expelled from the catalyst as hydrogen sulfide and the catalyst granules are sufficiently reactivated that hydrogen is liberated when a sample of granules of the catalyst is tested with 0.1 normal aqueous sodium hydroxide solution at 25° C.

2. A process for reactivating spent granular nickel-aluminum alloy catalysts, which have become deactivated through prolonged use and formation of a sulfur-containing film thereon, which comprises subjecting the said spent catalysts to the action of dilute aqueous nitric acid having a concentration of about 15% to 21% at a temperature of about 65° to 100° C, continuing the said treatment with the said dilute aqueous nitric acid until the sulfur has been expelled from the catalyst as hydrogen sulfide and the catalyst granules are sufficiently reactivated that hydrogen is liberated when a sample of granules of the catalyst is tested with 0.1 normal aqueous sodium hydroxide solution at 25° C, thereupon stopping the said reactivation treatment, and recovering the resultant reactivated catalyst granules from the reaction mixture.

3. A process for reactivating spent granular nickel-aluminum alloy catalysts, which have become deactivated through prolonged use and formation of a sulfur-containing film thereon, which comprises subjecting the said spent catalysts to the action of dilute aqueous nitric acid having a concentration of about 15% to 21% at a temperature of about 65° to 100° C, continuing the said treatment with the said dilute aqueous nitric acid until the sulfur has been expelled from the catalyst as hydrogen sulfide and the catalyst granules are sufficiently reactivated that hydrogen is liberated when a sample of granules of the catalyst is tested with 0.1 normal aqueous sodium hydroxide solution at 25° C, thereupon stopping the said reactivation treatment, and recovering the resultant reactivated catalyst granules from the reaction mixture.

4. A process for reactivating spent granular nickel-aluminum alloy catalysts, which have become deactivated through prolonged use and formation of a sulfur-containing film thereon, which comprises subjecting the said spent catalysts to the action of dilute aqueous nitric acid having a concentration of about 15% to 21% at a temperature of about 95° to 100° C, with vigorous mechanical agitation, continuing the said treatment with the said dilute aqueous nitric acid until the sulfur has been expelled from the catalyst as hydrogen sulfide and the catalyst granules are sufficiently reactivated that hydrogen is liberated when a sample of granules of the catalyst is tested with 0.1 normal aqueous sodium hydroxide solution at 25° C, thereupon stopping the said reactivation treatment, and recovering the resultant reactivated catalyst granules from the reaction mixture.

5. A process for reactivating spent granular nickel-aluminum alloy catalysts, which have become deactivated through prolonged use and formation of a sulfur-containing film thereon, which comprises vigorously agitating granules of the said spent catalyst with water, while gradually adding to the agitated mixture sufficient nitric acid to provide a dilute aqueous nitric acid of about 18% concentration, continuing the agitation of the mixture at a temperature within the range of about 95° to 100° C, until the catalyst has been expelled from the mixture as hydrogen sulfide and the catalyst granules are sufficiently reactivated that hydrogen is liberated when a sample of granules of the catalyst is tested with 0.1 normal aqueous sodium hydroxide solution at 25° C, thereupon stopping the said reactivation treatment, and recovering the resultant reactivated catalyst granules from the reaction mixture.

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