PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Revivification of Metallic Hydrogenation Catalysts

I, Edward Bradford Maxted, D.Sc., of 9, Alexanda Road, Bristol, 8, a British Subject, do hereby declare the nature of this invention to be as follows:—

It is well known that nickel or other metallic hydrogenation catalysts, on being used for the catalytic hydrogenation of impure materials containing catalyst poisons such as toxic sulphur compounds, lose their activity partially or substantially completely and thus become less effective for further use.

The present invention relates to the revivification of such catalysts, namely to treatment by means of which the catalytic activity of poisoned or partially poisoned metallic hydrogenation catalysts may be restored; and, in particular, the invention relates to the revivification of hydrogenation catalysts consisting of or containing metallic nickel, cobalt, copper or iron which have become partially or completely poisoned as a result of their previous use for the catalytic hydrogenation or reduction of impure materials containing catalyst poisons consisting of toxic compounds of sulphur, selenium, tellurium or phosphorus or of these elements in a free state. Of these poisons, toxic sulphur compounds constitute the type of catalyst poison most frequently met with in the materials normally hydrogenated in practice. Suitable catalysts for subjection to the revivification treatment hereinafter described include spent or partly spent catalysts consisting of or containing metallic nickel which have become partly or completely inactivated by previous use for the hydrogenation or reduction of impure organic substances, for example for the catalytic hydrogenation of unsaturated glycerides or for the hydrogenation of substances such as benzene, naphthalene or the phenols (including the cresols or xylenols); but the invention is not restricted to the revivification of poisoned or partially poisoned catalysts derived from these paticular reactions only; thus the revivification treatment may also, for example, be applied for the reactivation of catalysts containing nickel or cobalt which have become deactivated or poisoned by sulphur compounds as a result of their use for the catalytic reduction of impure carbon monoxide to liquid products or for the reactivation of catalysts consisting of or containing iron which have become poisoned by traces of sulphur as a result of their use in the synthesis of ammonia, which reaction may be regarded as involving the hydrogenation of elementary nitrogen.

The revivification process which forms the subject of the present invention consists essentially in the treatment of poisoned or partly poisoned hydrogenation catalysts, consisting of or containing metallic nickel, cobalt, copper or iron, with a reagent containing a peroxyacid or per-acid of molybdenum, tungsten, vanadium, chromium or phosphorus or a salt or other derivative of such peroxyacids or per-acids.

In general, the employment even of dilute solutions of reagents of the nature specified in the preceding paragraph is sufficient to cause an effective revivification of the poisoned catalyst; but the invention is not confined to the use of solutions of the above reagents having any special range of concentration nor to the use of such peroxyacids or per-acids or their derivatives made by any special method. It is however in many cases convenient to prepare the reagents containing the above peroxyacids or per-acids or derivatives of these by the action of hydrogen peroxide on a suitable salt or other compound containing molybdenum, tungsten, vanadium, chromium or phosphorus, in accordance with well known methods for making these peroxyacids or per-acids or their derivatives, and in this case the reagent as used may contain an excess of hydrogen peroxide in addition to the peroxyacid or per-acid of molybdenum, tungsten, vanadium, chromium or phosphorus (or the salt or other derivative of such peroxyacid or per-acid) which forms the essential part of the revivifying reagent.

If the metallic catalyst to be revived has previously been used for the hydrogenation of an impure organic material, it is in most cases advantageous to wash the poisoned catalyst with a suitable solvent to remove any adhering organic material prior to the application of the revivifying reagent; and a washing process may also be applied after revivification. Further, it may be necessary, after the revivification and after any subsequent washing, to re-reduce the revivified catalyst, for instance with hydrogen, before the re-use of the catalyst for catalytic hydrogenation.

The following example is given in order to illustrate a suitable way of carrying out the revivifying process in pactice; but the invention is of couse not limited to the materials or conditions employed in the example.

EXAMPLE 1.

The catalyst taken for revivification consisted of kieselguhr-supported nickel, which had originally been made by the reduction of basic nickel carbonate on kieselguhr with hydrogen at 300—320° Centigrade and which had become poisoned down to an activity of about two per cent of its original activity by being used in the hydrogenation of an impure phenol. The catalyst, in its poisoned state, was freed from adherent phenol first as far as possible by filtration and subsequently by thorough washing with hot water. It was then suspended in cold water and revivified by the addition, with stirring, of a revivifying reagent containing sodium peroxymolybdate in dilute aqueous solution, this peroxymolybdate being made in the usual manner by allowing sodium molybdate—in amount equal to about one per cent by weight of the poisoned nickel to be treated—to react with an excess of hydrogen peroxide. The aqueous suspension of the catalyst in the reagent was then heated to 100° C. in order to destroy any excess of peroxymolybdate, after which the catalyst was washed with water and dried at 100°C. On testing the revivified catalyst, after re-reduction with hydrogen at 300—320°C., it was found that the original activity had been restored. Thus, three comparative tests of the relative catalytic activity of, firstly, the original catalyst before being used for the hydrogenation of the impure phenol, secondly, the poisoned catalyst as received for revivification and, thirdly, the poisoned catalyst after revivification were made by using three equal small testing samples containing in each case about 0.08 gram of metallic nickel, for the hydrogenation of 10 c.c. of pure phenol in a hydrogenation shaker at atmospheric pressure and at 150°C. under standardised testing conditions, the volume of hydrogen absorbed during a 10 minute run being 178.1 c.c. for the original catalyst, 4.1 c.c. for the poisoned catalyst and 178.5 c.c. for the revivified catalyst.

Dated the 9th day of July, 1948.
E. B. MAXTED.

COMPLETE SPECIFICATION

Revivification of Metallic Hydrogenation Catalysts

I, EDWARD BRADFORD MAXTED, D.Sc., of 9, Alexandra Road, Bristol, 8, a British Subject, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

It is well known that nickel or other metallic hydrogenation catalysts, on being used for the catalytic hydrogenation of impure materials containing catalyst poisons such as catalytically toxic sulphur compounds, lose their catalytic activity for such hydrogenation partially or substantially completely and thus become less effective or ineffective for further use.

The present invention relates to the revivification of such catalysts, namely to treatment by means of which the catalytic activity of poisoned or partially poisoned metallic hydrogenation catalysts may be restored; and, in particular, the invention relates to the revivification of hydrogenation catalysts consisting of or containing metallic nickel, cobalt, copper or iron which have become partially or completely poisoned as a result of their previous use for the catalytic hydrogenation or reduction of impure materials containing catalyst poisons consisting of catalytically toxic compounds of sulphur, selenium, tellurium or phosphorus or of these elements in a free state. Of these poisons, toxic sulphur compounds constitute the type of catalyst poison most frequently met with in the materials normally hydrogenated in practice. Suitable catalysts for subjection to the revivification process hereinafter described include spent or partly spent catalysts consisting of or containing metallic nickel which have become partly or completely inactivated by previous use for the hydrogenation or reduction of impure organic substances, for example for the catalytic hydrogenation of unsaturated glycerides or for the hydrogenation of substances such as technical benzene, naphthalene or the phenols (including the cresols or xylenols); but the invention is not restricted to the revivification of poisoned or partially poisoned catalysts derived from these particular reactions only; thus the revivification treatment may also, for example, be applied for the reactivation of catalysts containing nickel, cobalt or iron which have become deactivated or poisoned by sulphur compounds as a result of their use for the catalytic reduction of impure carbon monoxide with hydrogen to liquid products or for the reactivation of catalysts consisting of or containing iron which have become poisoned by traces of sulphur or sulphur compounds as a result of their use in the synthesis of ammonia, which reaction may be regarded as involving the hydrogenation of elemetary nitrogen.

The revivification process which forms the subject of the present invention consists essentially in the treatment of poisoned or partly poisoned hydrogenation catalysts, consisting of or containing metallic nickel, cobalt, copper or iron, with a solution of a per-acid of molybdenum, tungsten, vanadium, chromium or phosphorus or a salt of such per-acids. Since the common per-acids of these elements are sometimes termed peroxyacids, the term per-acid in the present specification is to be understood to include the so-called peroxyacids of molybdenum, tungsten, vanadium, chromium or phosphorous, for example the term permolybdic acid, having as salts the permolybdates, is to be understood as synonymous with peroxymolybdic acid, having as salts the peroxymolybdates.

In general, the employment even of dilute solutions of reagents of the nature specified in the last preceding paragraph is sufficient to cause an effective revivification of the poisoned catalyst; but the invention is not confined to the uses of solutions of the above reagents having any special range of concentration nor to the use of such per-acids or their derivatives made by any special method. It is however in many cases convenient to prepare the solutions containing the above per-acids or salts of these by the action of hydrogen peroxide on a suitable acid, salt or other compound containing molybdenum, tungsten, vanadium, chromium, or phosphorus, in accordance with well known methods for making these per-acids or their salts, and in this case the solution as used may contain an excess of hydrogen peroxide in addition to the per-acid of molybdenum, tungsten, vanadium, chromium or phosphorus (or the salt of such per-acid) which forms the essential part of the revivifying reagent.

If the metallic catalyst to be revived has previously been used for the hydrogenation of an impure organic material, it is in most cases advantageous to wash the poisoned catalyst with a suitable solvent to remove any adhering organic material prior to the application of the revivifying reagent; and a washing process is also applied after revivification. Further, it may be necessary, after the revivification and after subsequent washing, to re-reduce the revivified catalyst, for instance with hydrogen, before the re-use of the catalyst for catalytic hydrogenation.

The following examples are given in order to illustrate the carrying out of the revivifying process in practice without however limiting the invention to the particular poisoned catalysts or the particular revivifying reagents or to the exact procedure given in these examples. It is to be noted that the present invention relates to the revivification of metallic catalysts which have previously been used in the catalytic hydrogenation of impure materials and not to the revivification of metallic adsorbents which have been used merely for the purification from catalyst poisons of substances which are subsequently to undergo catalytic hydrogenation, which latter process forms the subject of my Patent Application No. 18602, (Serial No. 644,240) of the same date as the present application.

Example 1.

The catalyst taken for revivification consisted of kieselguhr-supported nickel, which had originally been made by the reduction of basic nickel carbonate on kieselguhr with hydrogen at 300—320° Centigrade and which had become poisoned down to an activity of about two per cent of its original activity by being used in the hydrogenation of an impure phenol containing catalytically toxic sulphur compounds as the principal catalyst poisons. The catalyst, in its poisoned state was freed from adherent phenol first as far as possible by filtration and subsequently by thorough washing with hot water. It was then suspended in cold water and revivified by the addition, with stirring, of sodium permolybdate in dilute aqueous solution, this permolybdate being made in the usual manner by allowing sodium molybdate—in amount equal to about one per cent by weight of the poisoned nickel to be treated—to react with an excess of hydrogen peroxide. The aqueous suspension of the catalyst in the reagent was then heated to 100° C., in order to destroy any excess of permolybdate, after which the catalyst was separated, washed with water and dried at 100°C. On testing the revivified catalyst, after its re-reduction with hydrogen at 300—320°C., it was found that the original activity had been restored. Thus, three comparative small scale tests, in a laboratory testing apparatus, of the relative catalytic activity of, firstly, the original catalyst before being used for the hydrogenation of the impure phenol, secondly, the poisoned catalyst as received for revivification and, thirdly, the poisoned catalyst after revivification were made by using three equal small testing samples, containing in each case about 0.08 gram of metallic nickel, for the hydrogenation of 10 c.c. of pure phenol in a hydrogenation shaker at atmospheric pressure and at 150°C., under standardised testing conditions, the volume of hydrogen absorbed during a 10 minutes run being 178.1 c.c. for the original unpoisoned catalyst, 4.1 c.c. for the poisoned catalyst and 178.5 c.c. for the revivified catalyst.

EXAMPLE 2.

The catalyst taken for revivification was similar to that used in Example 1. The revivification was carried out in the manner already described in Example 1 save that a solution containing sodium perchromate, made by allowing a cold dilute solution of sodium chromate to interact with an excess of hydrogen peroxide, was used as the revivifying reagent.

EXAMPLE 3.

The catalyst subjected to the revivification process consisted in this case of a nickel catalyst similar to that in Example 1 save that it had become poisoned by its previous use for the hydrogenation of soya bean oil containing small quantities of catalytically toxic sulphur compounds. The catalyst, in its poisoned state, was freed from adherent hydrogenated oil, first as far as possible by filtration and subsequently by washing with boiling aqueous-alcoholic sodium hydroxide solution, followed by washing with hot aqueous-alcohol and subsequently by thorough washing with hot water. It was then suspended in cold water and revivified by the addition, with stirring, of a solution containing sodium permolybdate, made by the interaction of a cold dilute solution of sodium molybdate with an excess of hydrogen peroxide, the remainder of the revivifying treatment being similar to that already described in Example 1 save that the washing of the catalyst after the application of the revivifying reagent was carried out firstly with hot water, then with hot alcohol and, finally, thoroughly with hot water.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. A process of revivifying hydrogenation catalysts consisting of or containing metallic nickel, cobalt, copper or iron which have become partially or completely poisoned as a result of their previous use for the catalytic hydrogenation or reduction of impure materials containing catalyst poisons consisting of catalytically toxic compounds of sulphur, selenium, tellurium or phosphorus or of these toxic elements in a free state, which comprises treating the poisoned catalyst with a solution of a revivifying reagent comprising a per-acid of molybdenum, tungsten, vanadium, chromium or phosphorus, or a salt thereof, and subjecting the so-treated catalyst to washing and drying.

2. A process as in claim 1 wherein the catalysts have become partially or completely poisoned as a result of their previous use for the catalytic hydrogenation or reduction of impure benzene, naphthalene, phenol cresol, xylenol or unsaturated glycerides containing in each case catalytically toxic sulphur compounds as the principal catalyst poisons.

3. A process as in claim 1 wherein the solution of the per-acid of molybdenum, tungsten, vanadium, chromium or phosphorus, or a salt of such per-acids, is made by the interaction of hydrogen peroxide with a suitable acid or salt of molybdenum, tungsten, vanadium, chromium or phosphorus, the solution containing, if desired, an excess of hydrogen peroxide.

Dated the 5th day of August, 1949.

E. B. MAXTED.

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