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REACTIVATION OF SPENT HYDROGENATION CATALYSTS

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This invention relates to the reactivation of catalysts and in particular to a two-stage electrolytic reactivation of spent massive metal hydrogenation catalysts.

5 Prior to this invention it has been the practice to submit spent massive metal hydrogenation catalysts to anodic oxidation in dilute solutions of mild alkalis. The older practice required that the anodic oxidation process be preceded by washing the catalysts thoroughly with
10 organic solvents to remove completely the organic matter retained by the catalyst after use. Such organic matter constitutes a catalyst poison and reduces the activity of the catalyst
15 in the hydrogenation process. Expense arising from the use and recovery of solvents by the older practice is eliminated by the practice of the present invention.

We have found that a two-stage anodic oxidation of the catalyst is a more economical and more satisfactory process for the reactivation of spent massive metal catalysts than methods heretofore used. In this two-stage anodic oxidation process advantage is taken of the fact
25 that organic poisons retained by the catalyst after use may be oxidized easily in strongly alkaline electrolytic solutions. Very simple equipment and inexpensive solutions are required to accomplish the removal of the organic matter. Furthermore, the time required to remove the
30 organic matter from the catalyst by electrolytic oxidation is usually less than is required by the more costly solvent washing of the catalyst. After the removal of the organic matter by
35 anodic oxidation, the surface of the massive metal catalyst may be activated by anodic oxidation in mildly alkaline solutions. The activation step consists of forming a tightly adhering film of metallic oxide or peroxide on the surface of the massive metal. Reduction in an
40 atmosphere of hydrogen at elevated temperatures ordinarily completes the preparation of the catalyst for use.

The process to be illustrated below may be used for the reactivation of the well known massive
45 metal catalysts composed of such metals as copper, nickel, or cobalt or alloys of these metals with each other or with other metals such as chromium, platinum, palladium, iron, or aluminum, as well as mixtures of any of the above
50 metals and alloys.

The invention may be more clearly understood from the following detailed example: A massive
55 nickel catalyst such as nickel turnings, wire or chips, contained in a suitable wire basket or

cage, which has become spent through use in a hydrogenation process is placed in a solution of sodium hydroxide of about 6.5% concentration, although solutions of 4% to 10% sodium hydroxide concentrations are suitable. For convenience the catalyst is usually enclosed in a
5 cloth or canvas bag which serves as a diaphragm. The catalyst is made the anode of an electrolytic cell and a sheet of nickel is made the cathode of the cell. A current, whose density is 0.05 to 0.10
10 ampere per square inch as determined by assuming the surface of the catalyst to be a solid surface whose dimensions are the dimensions of the cage enclosing the catalyst, and at a potential of 4 to 10 volts, is passed through the cell.
15 The passage of the current will be accompanied by no evolution of oxygen from the anode as long as appreciable amounts of organic material remain on the catalyst. It is well to continue the anodic oxidation of the catalyst for an hour after the appearance of evolved oxygen.
20 The catalyst is washed with water and is then ready for the second stage of the process which comprises anodic oxidation in a solution of a mild alkali, such as a 2.5% solution of sodium carbonate in water or a saturated solution of calcium or strontium hydroxide, or even a dilute sodium hydroxide solution, say of 1/25,000% to 2%
25 concentration. It is well to surround the catalyst with another diaphragm, such as a cloth or canvas bag. The amperage and voltage of the current employed in the second stage are similar to those employed in the first stage. During the
30 second stage of the reactivation process, a film of tightly adhering black nickel oxide or peroxide is formed on the massive metal. Four to forty-eight hours may be required to complete the second stage of the reactivation process. At the conclusion of the second stage, the catalyst is washed with distilled water until free of alkaline material. Reduction of the oxide or peroxide to active catalytic nickel is accomplished
35 by heating in an atmosphere of hydrogen, preferably in the hydrogenation vessel, for 1 to 2 hours at a temperature of 200° to 250° C.
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Although the foregoing example of the invention has been given in considerable detail, it is understood that wide variation may be used with respect to materials and proportions of materials without departing from the scope and
50 spirit of the invention.

We claim:

1. A process for reactivating spent massive metal hydrogenation catalysts contaminated with organic materials which comprises subjecting the
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5 catalyst to electrolytic anodic oxidation in a strongly alkaline solution, then subjecting the catalyst to electrolytic anodic oxidation in a mildly alkaline solution, then washing the catalyst with water and finally reducing the catalyst in an atmosphere of hydrogen at an elevated temperature.

10 2. A process for reactivating spent massive metal hydrogenation catalysts contaminated with organic materials which comprises subjecting the catalyst to electrolytic anodic oxidation in a strongly alkaline solution of sodium hydroxide, then subjecting the catalyst to electrolytic anodic oxidation in a mildly alkaline solution, then washing the catalyst with water and finally reducing the catalyst in an atmosphere of hydrogen at an elevated temperature.

15 3. A process for reactivating spent massive metal hydrogenation catalysts contaminated with organic materials which comprises subjecting the catalyst to electrolytic anodic oxidation in a solution of sodium hydroxide of 4% to 10% concentration, then subjecting the catalyst to electrolytic anodic oxidation in a mildly alkaline solution, then washing the catalyst with water and finally reducing the catalyst in an atmosphere of hydrogen at elevated temperatures.

20 4. A process as defined by claim 3 in which the mildly alkaline solution is a solution of sodium carbonate of 1 to 5% concentration.

25 5. A process as defined by claim 3 in which the mildly alkaline solution is a saturated solution of an alkaline earth hydroxide.

30 6. A process as defined by claim 3 in which the mildly alkaline solution is a saturated solution of strontium hydroxide.

35 7. A process for reactivating spent massive metal catalysts contaminated with organic materials which comprises subjecting the catalyst to electrolytic anodic oxidation in a solution of sodium hydroxide of 4% to 10% concentration, then subjecting the catalyst to electrolytic anodic oxidation in a solution of sodium hydroxide of 1/25,000% to 2% concentration, then washing the catalyst with water and finally reducing the catalyst in an atmosphere of hydrogen at an elevated temperature.

40 8. A process as defined by claim 1 in which the catalyst is subjected to electrolytic anodic oxidation in a strongly alkaline solution until substantially all the organic matter has been oxidized off the catalyst as evidenced by a copious evolution of oxygen from the surface of the catalyst.

45 9. A process as defined by claim 1 in which the catalyst is subjected to electrolytic anodic oxidation in a mildly alkaline solution until a tightly adhering film of metallic oxide or peroxide has been formed on the surface of the massive metal.

50 10. A process as defined by claim 7 in which

the catalyst is subjected to electrolytic anodic oxidation in a solution of sodium hydroxide of 1/25,000% to 2% concentration until a tightly adhering film of metallic oxide or peroxide has been formed on the surface of the massive metal.

5 11. A process for reactivating spent massive nickel hydrogenation catalysts contaminated with organic materials which comprises subjecting the catalyst to electrolytic anodic oxidation in a solution of sodium hydroxide of about 6.5% concentration, until substantially all the organic matter has been oxidized off the catalyst as evidenced by a copious evolution of oxygen from the surface of the catalyst, then subjecting the catalyst to electrolytic anodic oxidation in a mildly alkaline solution until a tightly adhering film of metallic oxide or peroxide has been formed on the surface of the massive nickel catalyst, then washing the catalyst with water and finally reducing the catalyst in an atmosphere of hydrogen at an elevated temperature.

10 12. A process as defined by claim 11 in which the mildly alkaline solution is a solution of sodium carbonate of 1% to 5% concentration.

15 13. A process as defined by claim 11 in which the mildly alkaline solution is a saturated solution of an alkaline earth hydroxide.

20 14. A process as defined by claim 11 in which the mildly alkaline solution is a saturated solution of strontium hydroxide.

25 15. A process as defined by claim 11 in which the mildly alkaline solution is a solution of sodium hydroxide of 1/25,000% to 2% concentration.

30 16. A process for reactivating spent massive nickel hydrogenation catalysts contaminated with organic materials which comprises subjecting the catalyst to electrolytic anodic oxidation in a solution of sodium hydroxide of about 6.5% concentration until substantially all the organic matter has been oxidized off the catalyst as evidenced by a copious evolution of oxygen from the surface of the catalyst, then subjecting the catalyst to electrolytic anodic oxidation in a solution of sodium carbonate of about 2.5% concentration until a tightly adhering film of metallic oxide or peroxide is formed on the surface of massive catalyst metal, in both of which preceding electrolytic anodic oxidations the current has a density of 0.05 to 0.10 ampere per square inch as determined by assuming the catalyst surface to be the solid surface, the dimensions of which are the dimensions of the cage enclosing the catalyst, then washing the catalyst with water until substantially free of alkaline material and finally reducing the catalyst in an atmosphere of hydrogen for 1/2 to 4 hours at a temperature of 200° to 300° C.

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