

UNITED STATES PATENT OFFICE

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METHOD OF PREPARING CATALYTIC MATERIAL

No Drawing.

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My present invention relates to a method of preparing catalytic material such as may be used in the hydrogenation of oils, fats, waxes, and other hydrogenations and other catalytic reactions.

An object of the invention is to produce a catalytic material by the combination in an alloy of various proportions of a catalytic material and other material or materials, and also to produce materials having maximum catalytic properties by a novel method of treatment of such an alloy.

To this end the invention contemplates forming the alloy of a catalytic material and other material or materials, and treating the alloy with a gas such as hydrogen under suitable conditions of temperature and pressure and moisture in the gas, or moistening the powdered alloy after the gas treatment, whereby active catalytic material is produced.

The invention also contemplates treating the alloy with a solution of sodium carbonate to produce a catalytic material.

The invention further contemplates the treatment of the alloy with a solution of sodium carbonate and then treating the resultant catalytic product after washing substantially free from alkali, and either with or without separation from other by-products, and either wet or dry, with hydrogen gas under suitable conditions of temperature and pressure. The resultant solid end product is highly catalytic.

The invention also contemplates treating the alloy with sodium hydroxide or other solvent, which is a solvent of one or some only of the materials forming the alloy, in an amount insufficient to completely dissolve that material, the resulting product, after washing substantially free from alkali, having catalytic properties.

The catalytic properties of this material may be further enhanced by treatment with hydrogen gas, under suitable conditions of temperature and pressure.

The invention further contemplates treating the alloy in cold water, or hot water, in water at the boiling point at atmospheric

pressure, or in hot water or steam under pressure. The invention also contemplates in general, the treatment of the alloy with water which has had its boiling point raised by the addition of sugar, salt, and various other water soluble salts or compounds, that would in effect raise the boiling point of the water and thereby subject the alloy to a higher temperature without or independently of the application of pressure.

The catalytic properties of the material resulting from the aqueous treatment may be enhanced by treatment with hydrogen gas under suitable conditions of temperature and pressure.

I preferably use nickel as the primary or catalytic material of the alloy, although the invention contemplates also iron, copper, cobalt and other catalytic materials. As the secondary or other material of the alloy, which material may be non-catalytic, I preferably use aluminum or silicon although other materials may be used.

In carrying out the invention with nickel as the catalytic material and aluminum as the other material or one of the other materials, as there may be others, the nickel and aluminum with or without other materials, are alloyed together by melting, either separately or together, and combining in a suitable vessel in proportions ranging from 10% to 85% of nickel and from 90% to 15% of aluminum.

After the melt has fused and been thoroughly commingled, it is allowed to cool and is then broken into small pieces or pulverized to a powder in any desired apparatus.

This broken alloy may then be subjected in any desired apparatus to the action of hydrogen gas under suitable conditions of temperature and pressure, preferably above atmospheric pressure and normal temperature. I have found approximately twenty pounds per square inch and 300° F. to be very desirable conditions. The flow of hydrogen gas is preferably maintained for a considerable time, approximately four hours giving good results, and preferably moisture should be present and may be provided in

the gas, or the powdered alloy may be moistened or quenched after the gas treatment.

This hydrogen treatment results in a product having strong catalytic properties.

5 I have also found that when the nickel aluminum alloy, as above produced, is subjected to the action of a solution of sodium carbonate preferably at a boiling temperature, the sodium carbonate solution being at any
10 concentration up to saturation, a catalytic material is produced. I am not aware of the exact chemical reaction which takes place at this point, but the resultant product is extremely voluminous, due probably to the re-
15 action between the alkali and the aluminum, although the nickel may possibly enter into the reaction. This solid product, to wit, the result of the reaction between the alkali solution and the alloy, and after washing substantially free from alkali and with or without separation from other by-products and
20 impurities, is catalytic and may be used in the hydrogenation of oils or other hydrogenations or other catalytic reactions.

25 My experiments with different strengths of alkali in the solution used for digesting the nickel aluminum alloy lead to the discovery that the aluminum is changed into an insoluble compound of aluminum such as aluminum hydrate $\text{Al}_2\text{O}_3(3\text{H}_2\text{O})$ and is left with the nickel or other catalytic material to form a voluminous catalytic substance. It may be that the sodium carbonate raises the boiling point of the solution which makes
35 more effective the reaction between the aluminum and the water in the solution to produce the aluminum hydrate as follows:—



40 Whether the sodium carbonate reacts with the aluminum or not, the resultant voluminous material contains an insoluble material in addition to the nickel and is actively catalytic.

45 This catalytic product may be separated or not from other products or materials, and subjected, either in the wet or dry state, to the action of hydrogen gas under approximately similar conditions of temperature and
50 pressure for approximately the same period of time as suggested above. The resultant end product is of an active catalytic and voluminous nature.

A voluminous catalytic material may also
55 be produced by replacing the sodium carbonate in the above instances by a solution of sodium hydroxide or other solvent of the aluminum, insufficient in amount to completely dissolve the aluminum of the alloy, the resultant product, after washing substantially
60 free from alkali, being of voluminous nature and having catalytic properties.

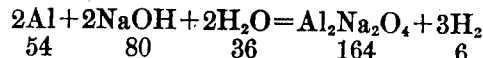
This voluminous catalytic product resulting from the treatment with the amount of
65 solvent insufficient to dissolve all of the alu-

minum, may be further treated for enhancement of catalytic properties by the hydrogen gas treatment under suitable conditions of pressure and temperature.

Reference is made to the treatments with
70 caustic soda to dissolve substantially all of the aluminum or other non-catalytic material to leave the catalytic material in finely divided condition as set forth in my Patents 1,563,587 of Dec. 1, 1925 and 1,628,190 of May
75 10, 1927.

According to the present invention an amount of caustic soda insufficient to dissolve all of the aluminum is used. One example of the treatment of the present invention would
80 be to use enough caustic soda to dissolve all but say 5% to 10% of the aluminum which would remain in the catalytic material as metallic aluminum probably mixed with aluminum hydrate. Another example would be
85 to use caustic soda in such quantity that 40% to 50% of the aluminum remains undissolved. In this example the aluminum would be left largely as aluminum hydrate. In both cases a voluminous catalytic material is
90 obtained.

The equation showing the reaction of aluminum with caustic soda may be shown as follows:



From this equation the theoretical weight of
caustic soda required to convert aluminum
100 into sodium aluminate is 1.48 times the weight of the aluminum, or for every pound of aluminum there is required 1.48 pounds of caustic soda. If only 90% of the alumi-
105 num was to be converted into sodium aluminate we would use 1.33 pounds of caustic per pound of aluminum. If we were to use .74 pound of caustic per pound of aluminum theoretically one half of the aluminum
110 would be converted into sodium aluminate. But the unconverted part would be changed into aluminum hydrate by the water. In actual practice caustic soda in excess of the theoretical amounts would be used to obtain
115 the results illustrated.

I have discovered that I can obtain a voluminous catalytic material similar to that produced by the treatment of the nickel aluminum alloy with sodium carbonate and the treatment with insufficient sodium hydroxide
120 or caustic soda, by using unheated water alone, or heated water at atmospheric pressure or greater, or steam under pressure or at atmospheric pressure, and in general with water which has had its boiling point raised
125 by the addition of sugar, salt and various other water soluble compounds.

Treatment with cold or unheated water, that is water at normal temperature of say
130 about 70° Fahrenheit is effective but requires

a longer time than water at say 180° Fahrenheit.

In preparing the catalyzer with water the nickel aluminum powder may be boiled in water at atmospheric pressure. This treatment is rather slow and may require a number of hours. In the treatment with water the finely divided aluminum apparently reduces the water, liberating the hydrogen in the water and uniting with the oxygen to form aluminum hydrate which reaction may be shown as follows:



The hotter the water the quicker the action. For working at atmospheric pressure the boiling point of the water may be raised by adding various water soluble compounds such as sugar, ordinary salt, and calcium chloride, but I find that although the addition of these materials will raise the boiling point of the water the reaction with the aluminum powder is not as materially accelerated as with the use of sodium bicarbonate added to the water.

A very much more effective and convenient way for raising the boiling point is to digest the nickel aluminum powder in a closed vessel with water or steam under pressure. This is accomplished simply by putting the powder and water in a suitable vessel and introducing steam directly into the vessel or heating the contents in any other convenient way. During the digesting operation the tank is vented enough to discharge the hydrogen which is generated.

It is to be noted that in the foregoing discussion covering the treatment that converts the aluminum into aluminum hydrate I have shown that this compound carries three molecules of water. For some purposes it is desirable that most of this water of crystallization be removed and it is sometimes necessary to heat the catalyzer containing the aluminum hydrate under hydrogen gas at a temperature which may run as high as 700° F. All of the water would not be driven off at this point and when any operation required that substantially all of this water be driven off the catalyzer material containing aluminum hydrate might have to be heated in air to a temperature as high as 1500° F.

After being exposed to air at this temperature substantially all of the water would be driven off but at the same time other changes would take place and the material would no longer be catalytic without subsequent treatment as follows.

The material which had been heated up to 1,500° F. in the air would then be placed in a suitable vessel and treated with hydrogen at a temperature between 500° and 600° F. until the escaping gas would not show the presence of any moisture. The moisture in

the escaping gas in this stage would be formed by the reducing action of the hydrogen on any reduceable oxides that were formed during the heating operation in air.

I do not desire to be limited to the temperatures given as conditions may require less or greater temperatures to drive off the water from the aluminum hydrate. Also I do not want to claim that the aluminum hydrate is in any sense an inactive material. In other words, it is not intended to be simply a support or carrier for the nickel but according to my best judgment and belief does contribute to the catalytic value.

I do not desire to limit the invention to aluminum as the non-catalytic material or other material, nor to nickel as the catalytic material, nor to the solvents mentioned, as other materials may be used within the scope of the invention.

The material need not necessarily be pulverized to a fine powder but it is good practice to prepare a given weight of the catalytic material in a form having as large a surface as possible particularly when the catalytic material is to be used in a liquid medium. For use with gases it is necessary to have the catalytic material in pieces large enough to keep them from being carried out of the reacting chamber by the gases. To accomplish this result with precipitated catalyzers which are usually in a finely divided state, it is necessary to bind the catalyzer with some porous type of cement.

In addition to use in hydrogenation of oils, fats, and waxes, the catalytic material, produced according to my methods above set forth, may be used in other hydrogenations such as gaseous hydrocarbons, and nitrogen.

The chemical equations that I have given are meant to show comparative results. I do not know that these equations might not be subject to criticism by more experienced chemists and might not be considerably modified. However, they serve the purpose for which they are intended and even though the equations might be changed the relative reactions would still hold true.

I claim:

1. A process of preparing catalytic material which consists in forming an alloy of a catalytic material with another material, and treating the alloy with hydrogen gas under elevated temperature and pressure, and in the presence of moisture.

2. A process of preparing catalytic material which consists in forming an alloy of catalytic material with another material, reducing the alloy to a powder and treating the powdered alloy with hydrogen gas under elevated temperature and pressure and in the presence of moisture.

3. A process of preparing catalytic material which consists in forming an alloy of a catalytic material with another material, re-

ducing the alloy to a powder, treating the powdered alloy with hydrogen gas at a temperature of approximately 300° F. and a pressure of approximately twenty pounds per square inch, and quenching the resultant product in water.

4. A process of preparing catalytic material which consists in alloying nickel with aluminum, reducing the alloy to a powder and treating the nickel aluminum powder with hydrogen gas under elevated temperature and pressure and in the presence of moisture.

5. A process of preparing catalytic material which consists in forming an alloy of a catalytic material with another material, and treating the alloy with sodium carbonate solution.

6. A process of preparing catalytic material which consists in forming an alloy of a catalytic material with another material, pulverizing the alloy, and treating the powdered alloy with sodium carbonate solution.

7. A process of preparing catalytic material which consists in forming an alloy of a catalytic material with another material, pulverizing the alloy, treating the powdered alloy with sodium carbonate solution, and washing the resultant product substantially free from the alkali.

8. A process of preparing catalytic material which consists in alloying nickel with aluminum, and treating the alloy with sodium carbonate solution.

9. A process of preparing catalytic material which consists in alloying nickel with aluminum, pulverizing the alloy, treating the powdered alloy with sodium carbonate solution, and washing the resultant product substantially free from alkali.

10. A method of preparing catalytic material which consists in alloying nickel and aluminum, treating the resultant alloy with sodium carbonate in solution, and then separating the solid material from the supernatant liquid.

11. A process of preparing catalytic material which consists in forming an alloy of a catalytic material with another material, treating the alloy with sodium carbonate solution, and treating the resultant solid material with hydrogen gas.

12. A process of preparing catalytic material which consists in forming an alloy of catalytic material with another material, reducing the alloy to a powder, treating the powdered alloy with sodium carbonate solution, washing substantially free from alkali, and treating the resultant solid material with hydrogen gas.

13. A process of preparing catalytic material, which consists in alloying nickel and aluminum, treating the resultant alloy with a solution of sodium carbonate, and then sub-

jecting the solid material so produced to the action of hydrogen gas.

14. A process of preparing catalytic material, which consists in alloying nickel and aluminum, treating the resultant alloy with a solution of sodium carbonate, and then subjecting the solid material so produced to the action of hydrogen gas under heat and pressure.

15. A process of preparing catalytic material, which consists in alloying nickel and aluminum, treating the resultant alloy with a solution of sodium carbonate, and then subjecting the solid material so produced to the action of hydrogen gas while wet.

16. A process of preparing catalytic material which consists in forming an alloy of a catalytic material with another material, and treating the alloy with a solvent only of said other material insufficient in amount to completely dissolve said other material.

17. A process of preparing catalytic material which consists in forming an alloy of a catalytic material with other material, reducing the alloy to a powder, and treating the powdered alloy with a solvent only of said other material insufficient in amount to completely dissolve said other material.

18. A process of preparing catalytic material which consists in alloying nickel with aluminum, reducing the alloy to a powder and treating the powdered alloy with a solvent only of the aluminum insufficient in amount to completely dissolve said aluminum.

19. The process of preparing catalytic material which consists in alloying nickel with aluminum, reducing the alloy to a powder, and treating the powdered alloy with sodium hydroxide solution insufficient in amount to completely dissolve said aluminum.

20. The process according to claim 16 including the steps of washing substantially free from alkali and treating with hydrogen gas under elevated temperature and pressure and in the presence of moisture.

21. A process according to claim 19 in which the amount of sodium hydroxide is such as to leave approximately five to ten per cent of the aluminum undissolved.

22. A process according to claim 19 in which the amount of sodium hydroxide is such as to leave approximately forty to fifty per cent of the aluminum undissolved.

23. A process of preparing catalytic material which consists in forming an alloy of a catalytic material with another material, pulverizing the alloy, treating the powdered alloy with heated water or steam with pressure to produce a catalyzer, and heating the catalyzer under hydrogen to a temperature such as to drive-off some of the water and to enhance the activity of said catalyzer.

24. A process of preparing catalytic material which consists in alloying nickel with

aluminum, reducing the alloy to powder, boiling the powdered alloy in water to produce a voluminous catalyzer.

25. The process of claim 24 in which the boiling of the powdered alloy in water is carried on under pressure.

26. The process of claim 24 in which the water contains a material in solution to raise the boiling point, said material being inactive with respect to the nickel.

27. A process of preparing catalytic material which consists in alloying nickel with aluminum, reducing the alloy to powder, treating the powdered alloy with heated water or steam under pressure to produce a voluminous catalyzer, heating the catalyzer under hydrogen to a temperature such as to drive off some of the water of crystallization associated with the aluminum, heating the catalyzer in air to a higher temperature required to drive off substantially all of the water, and then heating under hydrogen again.

28. A process of preparing catalytic material which consists in alloying nickel with aluminum, reducing the alloy to powder, treating the powdered alloy with heated water, or steam under pressure to produce a voluminous catalyzer, heating the catalyzer in air to a high temperature required to drive off substantially all of the water, and then heating under hydrogen.

29. The process of preparing catalytic material which consists in forming an alloy of a catalytic material with another material, reducing the alloy to powder, and boiling the powdered alloy in water to produce a catalyzer.

30. The process of claim 29 in which the water contains a substance in solution to raise the boiling point, said substance being inactive with respect to the nickel.

31. A process of preparing catalytic material which consists in forming an alloy of a catalytic material and another material, and partially dissolving said other material with a non-acidic solvent therefor, said solvent being inactive with respect to the catalytic material, leaving the catalytic material in a finely divided state.

32. A process of preparing catalytic material which consists in forming an alloy of a catalytic material and another material, and partially separating said other material from the catalytic material with a solution of a non-acidic substance chemically reactive with the said other material and inactive with respect to the catalytic material.

In testimony whereof, I affix my signature.

MURRAY RANEY.