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PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Production of Improved Metallic Compositions

We, WALTER HENRY GROOMBRIDGE and JOHN EDWARD NEWNS, both British subjects, of the Works of British Celanese Limited, Spondon, near Derby, do hereby declare the nature of this invention to be as follows:—

This invention relates to new or improved metallic compositions and more particularly compositions suitable for use as catalysts in chemical processes.

According to the invention a metal which is to be used as catalyst in a chemical process is supported upon another metal, the support metal having a porous structure and being permeated with the catalyst metal.

The novel catalyst compositions of the invention may be produced by a process which comprises heating an intimate mixture of the catalyst metal with the oxide of the metal which is to form its support to a high temperature and thereafter subjecting the product to reduction.

The metal which is to form the support of the catalyst mass must (as is the case with most metals) have a density greater than that of its oxide and should be reducible at a temperature sufficiently low to avoid fusion or excessive sintering of the resulting metal. Copper is of outstanding importance as the metal to form the support of the catalyst and offers the advantage of being relatively inert in most chemical reactions; iron may also be employed in this connection.

The metal and metal oxide are intimately mixed before being heated and to this end it is preferred to employ the substances in a very fine state of division. Thus, the metal may be employed in the form of very fine filings and the oxide as a finely ground powder. The substances may be employed in about equal proportions by weight, but this is not essential, for instance the proportions may be such that the product contains substantially more of the metal forming the support than of the metal with which it is permeated.

The temperature to which the mixture of metal and oxide is heated is preferably above 500° C., temperatures of 750—850 or even higher, e.g. 900° C., giving excellent results. The product obtained is hard but can be broken into particles or granules of a size suitable for use as a catalyst by an ordinary milling operation. After milling and grading, the product is subjected to reduction and usually it is convenient to effect the reduction with a commercial carbon monoxide-hydrogen mixture such as water gas or producer gas. The reduction should not be carried out at such a high temperature as to cause fusion or excessive sintering of the product and a reducing temperature not exceeding about 500° C. is to be preferred.

In the reduced product the supporting metal is in a highly porous form and is permeated by the catalytically active metal. The thoroughness of the permeation depends to a large extent upon the care taken in effecting intimate admixture of the starting materials and upon the conditions obtaining during the heat treatment. The employment of the catalyst metal in the free state and the supporting metal as an oxide may lead to a high degree of permeation as a result of the transference of oxygen from the oxide of the supporting metal to the catalyst metal during the heating; in this connection it is to be noted that it is preferred to employ a higher oxide of the supporting metal for starting material, e.g. cupric oxide or ferric oxide. On the other hand the catalyst metal need not be employed in the free state and the production of the catalyst may involve simply the formation, heating and reduction of an intimate mixture of metal oxides.

The production of the oxide or oxides in a fine state of division may be effected by grinding or may involve precipitation of a compound of the metal or metals from solution, for instance the precipitation of a hydroxide from a solution of a metal salt. Where a mixture of metal oxides is to be employed co-precipitation affords a ready method of obtaining thorough admixture. Compounds formed by precipitation, e.g. hydroxides or carbonates, may be employed as such in the process of the invention, especially when they are transformed into oxides by

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heat at relatively low temperatures.

In use as a catalyst the reduced product is remarkable for its lack of friability and may be used for considerable periods without disintegration. Even repeated changes in temperature, for instance when the catalytic process is interrupted for regeneration or reactivation of the catalyst do not cause serious damage to the catalyst. A highly porous nature and hence a high surface : volume ratio and a high thermal conductivity are valuable features of the novel catalysts.

An important embodiment of the present invention is the production of catalysts containing nickel and/or cobalt supported on copper or iron, and the use of these catalysts in hydrogenation processes, especially the hydrogenation of oxides of carbon to produce hydrocarbons. The invention may, however, be applied to the production of catalysts for use in other processes, for instance the production of acetone from ethyl alcohol, and it is to be noted that in the application of the novel catalysts the invention is not limited to the employment as support of a metal which is inert catalytically and both the support metal and the metal or metals with which it is permeated may have a catalytic effect in the process in which the catalyst is employed. Furthermore, besides the metal forming the support and the metal or metals with which it is permeated, other substances may be incorporated in or applied to the novel metallic compositions. Such other substances may be applied after or incorporated at any stage during the production of the composition; for instance, in producing catalysts suitable for synthesising hydrocarbons from oxides of carbon and hydrogen a substance such as thorium oxide may be applied to or incorporated in the composition, while in the production of acetone from ethyl alcohol a catalyst having iron as the supporting metal may be subjected to conditions which cause superficial rusting of the iron and/or calcium acetate may be applied to the catalyst.

Dated this 8th day of December, 1937.

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COMPLETE SPECIFICATION

Production of Improved Metallic Compositions

We, Walter Henry Groombridge and John Edward Newns, both British subjects, of the Works of British Celanese Limited, Spondon, near Derby, 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:—

This invention relates to the production of improved metallic compositions suitable for use as catalysts for the hydrogenation of carbon compounds, and to the use of the metallic compositions in the hydrogenation of carbon compounds.

The metallic compositions of the invention are made by heating an intimate admixture of a heavy metal oxide with another heavy metal of higher affinity for oxygen so as to obtain a porous structure of one heavy metal oxide permeated with, and serving as the support for, an oxide of the other heavy metal and reducing said porous structure by means of a gaseous reducing agent to form a porous substantially non-friable structure of the heavy metal of lower affinity for oxygen permeated with, and serving as the support for, the heavy metal of higher affinity for oxygen.

The metal oxide should be reducible at a temperature sufficiently low to avoid fusion or excessive sintering of the resulting metal. Copper oxide is of outstanding importance as the oxide with which to heat the metal of higher affinity for oxygen.

The metal and metal oxide are intimately mixed before being heated and to this end it is preferred to employ the substances in a very fine state of division. Thus, the metal may be employed in the form of very fine filings and the oxide as a finely ground powder. The substances may be employed in about equal proportions by weight, but this is not essential, for instance the proportions may be such that the product contains substantially more of the metal of lower affinity for oxygen than of the metal of higher affinity with which it is permeated.

The temperature to which the mixture of metal and oxide is heated is preferably above 500° C., temperatures of 750—850° C. or even higher, e.g. 900° C., giving excellent results. The product obtained is hard but can be broken into particles or granules of a size suitable for use as a catalyst by an ordinary milling operation. The product, preferably after milling and grading, is subjected to reduction and usually it is convenient to effect the reduction with a commercial carbon monoxide-hydrogen mixture such as water gas or producer gas. The reduction should not be carried out at such a high temperature as to cause fusion or excessive sintering of the product. Reducing temperatures between about 300 and 700° C., e.g. 350—500° C. depending on the nature of the metal of higher affinity for oxygen, may be mentioned.

In the reduced product the metal of lower oxygen affinity is in a highly porous form and is permeated by the metal of higher affinity. The thoroughness of the permeation depends to a large extent upon the care taken in effecting intimate admixture of the starting materials and upon the conditions obtaining during the heat treatment. The high degree of permeation obtainable may be at least in part a result of the transference of oxygen from the oxide of the one metal to the other metal during the heating and it is preferred that the oxide employed in the initial mixture should be a higher oxide, e.g. cupric oxide.

In use as a catalyst the reduced product is remarkable for its lack of friability and may be used for considerable periods without disintegration. Even repeated changes in temperature, for instance when the catalytic process is interrupted for regeneration or reactivation of the catalyst do not cause serious damage to the catalyst. A highly porous nature and hence a high surface : volume ratio and a high thermal conductivity are valuable features of the novel catalysts.

An important embodiment of the present invention is the production of catalysts wherein the metal of higher affinity for oxygen is nickel or cobalt and the metal of lower affinity for oxygen is copper, and the use of these catalysts in hydrogenation processes, especially the hydrogenation of oxides of carbon to produce hydrocarbons. The invention may, however, be applied to the production of catalysts for use in other processes, for instance the production of acetone from ethyl alcohol. The compositions of the invention may be employed in processes wherein both the heavy metals present contribute to catalyse the reaction. Moreover, the compositions may be employed in reactions in which the metals present play the part of reagents rather of catalysts in the strict sense, e.g. in combining with and removing oxygen and halogens from compounds.

The following Examples illustrate the production of a metallic composition according to the invention:—

EXAMPLE 1.

An intimate mixture of equal parts by weight of copper oxide and nickel powder is heated in a fire-clay crucible to about 900° C. The copper oxide is thereby reduced to the cuprous state with corresponding oxidation of the nickel. The resulting substantially homogeneous mass is broken into pieces of $\frac{1}{8}''$—$\frac{1}{4}''$ mesh and reduced in a current of water gas at about 350° C. The resulting composition is suitable for use as a catalyst in the reduction of carbon monoxide to a hydrocarbon, for example methane.

EXAMPLE 2.

The process is carried out as in Example 1 but substituting powdered cobalt for powdered nickel.

The following Example illustrates the use of the compositions of the invention in the reduction of carbon monoxide.

EXAMPLE 3.

Each of a number of externally heated copper tubes is charged with the composition obtained according to Example 1. A mixture of carbon monoxide and hydrogen in molecular proportions of 1:3 respectively is passed through the tubes at a space velocity of 70. The issuing gas contains methane in a proportion corresponding to a 30% conversion.

Instead of the composition of Example 1, that of Example 2 may be used.

Besides the heavy metals, other substances may be incorporated in or applied to the novel metallic compositions. Such other substances may be applied after or incorporated at any stage during the production of the composition; for instance, in producing catalysts suitable for synthesising hydrocarbons from oxides of carbon and hydrogen, a substance such as thorium oxide may be applied to or incorporated in the composition.

The production of substantially non-friable metallic compositions suitable for use in the production of hydrogen by decomposition of steam or water under the influence of heat by heating an intimate mixture of finely divided copper oxide and iron to bring about reduction of copper oxide to cuprous oxide by the iron, and subsequently subjecting the resulting composition to the action of a reducing atmosphere to reduce the metallic oxides to the corresponding metals, as well as the composition so produced are claimed in Specification No. 34125/37. The said Specification further claims the use of the said compositions in the production of hydrogen by the decomposition of steam or water by the action of heat. We do not claim such production of copper-iron compositions, compositions so produced or their use in the present Specification.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that, subject to the foregoing disclaimer, what we claim is:—

1. Process for the production of a substantially non-friable metallic composition useful as a catalyst for the hydrogenation of carbon compounds, which comprises forming a porous structure of an oxide of one heavy metal permeated with, and serving as the support for, the oxide of another heavy metal having a higher affinity for oxygen, by heating an intimate mixture of the second metal with the oxide of the first metal, both oxides being reducible to the respective metals by means of a gaseous reducing agent, and thereafter reducing the resulting composition by means of a gaseous reducing agent.

2. Process according to Claim 1, wherein the composition is mechanically reduced to a convenient size for use as a catalyst or contact reagent before reduction to the metallic state.

3. Process according to Claim 1 or 2, wherein the metal of lower affinity for oxygen is copper.

4. Process according to any of Claims 1—3, wherein the metal of higher affinity for oxygen is cobalt.

5. Process according to any of Claims 1—3, wherein the metal of higher affinity for oxygen is nickel.

6. Process for the production of a substantially non-friable metallic composition useful as a catalyst for the hydrogenation of carbon compounds, substantially as hereinbefore described.

7. A substantially non-friable metallic composition useful as a catalyst for the hydrogenation of carbon compounds when produced by any of the processes hereinbefore described and claimed.

8. Process for the hydrogenation of carbon compounds, which comprises reacting the compound at an elevated temperature with hydrogen in the presence of a metallic composition claimed in Claim 7.

9. Process for the hydrogenation of carbon monoxide, which comprises reacting the carbon monoxide with hydrogen at an elevated temperature in contact with a metallic composition as claimed in Claim 7.

10. Process for the hydrogenation of carbon compounds substantially as hereinbefore described.

Dated this 10th day of November, 1938.
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