PATENT SPECIFICATION

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COMPLETE SPECIFICATION

New Catalyst of High Mechanical Strength

I, HAROLD EDWIN POTTS, Chartered Patent Agent, of 12, Church Street, Liverpool, in the County of Lancaster, Subject of the King of Great Britain, do hereby declare the nature of this invention which has been communicated to me by International Hydrogenation Patents Company Limited, a Company organised under the laws of Liechtenstein, of Vaduz, Liechtenstein, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

In catalytic processes in which high temperature, e.g. upwards of about 480° C., and up to about 1090° C., and flowing streams of reactants are employed, considerable difficulty is encountered with the catalyst when it is employed as a packing for the reaction zone. In such processes catalysts which have been found to be particularly effective have frequently proved to be lacking in mechanical strength and therefore to disintegrate too rapidly.

In order to strengthen such catalysts it has been the custom to deposit them on solid carriers of sufficient mechanical strength such as pumice, quartz, metal balls, etc. This procedure has the disadvantage that in such catalysts there is only a thin layer of active material which is liable to peel off even after a relatively short time of usage.

My foreign correspondents have found that catalysts of high mechanical strength, adapted for reactions conducted at high temperatures, are produced without the employment of solid carriers, by forming into pieces by compressing under high pressure of at least 500 atmospheres a finely divided compounded material, comprising an effective catalytic substance and the melting point of which is substantially higher than the temperature in the subsequent heating, or which forms a substance of said melting point in the subsequent heating, and heating the pieces to a temperature of at least 850° C., preferably of at least 920° C. The heating is performed for a sufficiently long time to effect a substantial increase in strength, preferably by causing the high melting compound to be formed in sufficient amounts to exercise a binding effect. The expression "compounded material" is intended to mean a material in which chemical compounds are present as essential ingredients.

As finely divided compounded material a powder is usually employed preferably in the dry state, although moist materials, for example moist powders or pastes may also serve for this purpose.

The pieces resulting from said heating treatment are advantageously crushed after cooling down, for example, to atmospheric temperature, to form a powder, which, in turn, is again compressed into pieces under high pressure of at least 500 atmospheres, the pieces obtained being likewise heated to a temperature of at least 850°, preferably of at least 920° Centigrade.

If the initial finely divided compounded material is in a moist state, for example, when it has been obtained by a precipitation from an aqueous solution or suspension or by the interaction of an aqueous solution or suspension with a reactant, or also if the initial material contains water of crystallisation, the moist material may first be formed into pieces by shaping, cutting and/or comparatively slight pressing and the like and the resulting pieces may then be heated to a comparatively low temperature, usually above 100° Centigrade, in order to expel the water contained therein, said temperature ranging up to about 400° Centigrade according to the material treated. The dry pieces are then subjected to compression under a pressure of at least 500 atmospheres according to the present invention and heated to the aforesaid high temperature of at least 850° Centigrade.

In addition to the said drying or roasting step, a reducing treatment may be included either before or after the final heating, according to the material treated. For example, in the case of a catalyst containing nickel as an effective catalyst substance, the pieces of catalyst material may be subjected to a treatment in a reducing atmosphere or in a current of reducing gases such as hydrogen or ammonia at elevated temperature of say 150 to 660° Centigrade, so as to reduce any nickel oxide present to metallic nickel.

If the initial materials are already present in the form of solid pieces, these are crushed to form small granules or powder and further treated in accordance with the present invention.

It is especially useful, in accordance with the present invention, to mix a material comprising an effective catalytic substance with a substance capable of interacting with said material to form a compound having a melting point substantially higher than the temperature in the subsequent heating step, the mixture being heated to a temperature at least sufficient to cause said compound to be formed; when the compound is formed, the resulting product is crushed, if desired, to produce the finely divided material which is compressed into pieces under high pressure of at least 500 atmospheres and further heated in accordance with the present invention.

The types of substances which are capable of reacting with each other to form high melting compounds may be divided into two general classes; those which combine by reason of one being acidic and the other being basic in character and those which combine with each other to form double compounds of an additive nature. As illustrative of the first type may be mentioned magnesia and alumina which combine to form magnesium aluminate. As illustrative of the second group may be mentioned magnesia and sodium fluoride which are capable of combining to form a double fluoride.

The reactive substances added or at least one of them will in some cases have a melting point not in excess of about 810° Centigrade and this is desirable in order that the admixture and reaction of the reactive components may be facilitated. By far the greater number of reactive substances, however, have melting points higher than 810° Centigrade.

Wherever in the specification or in the appended claims an acidic substance is mentioned, this is intended to mean a substance which, in aqueous solution or suspension, gives an acid reaction or which, in a chemical compound, constitutes all or part of the anion. Wherever a basic substance is mentioned, this means a substance which, in aqueous solution or suspension, gives an alkaline reaction or, in a chemical compound, constitutes all or part of the cation.

As examples of acid substances may be mentioned amphoteric oxides such as alumina, oxides and acids of metals of group 6 of the periodic system, silica, oxides of bismuth, tin, lead, antimony, cobalt, arsenic, and vanadium, and oxides and acids of phosphorus and boron.

As examples of basic substances to be used in the practice of the present invention may be mentioned the oxides and other compounds of the alkaline earth metals, including magnesium, and oxides and other compounds of the alkali metals where the latter are not objectionable in the catalyst.

Typical of the substances which will combine with metal oxides to form double compounds are fluorides such as sodium fluoride and silicates such as sodium silicate.

The substances added to the catalyst should preferably be employed only in such an amount that the compound formed by the reaction constitutes a minor component of the catalyst, preferably not more than 10 per cent. thereof. The reason for this is that too extensive a reaction between such substances serves to effect a partial, often substantial reduction in the activity of the catalyst while only a relatively low degree of reaction will impart the desired strength. In most cases one of these reactive substances is already present in the catalyst, usually as a major component thereof, thereby necessitating the addition of only a small amount of the other reactive component in order to effect the process in accordance with the present invention.

Satisfactory strength can be imparted to catalysts composed of one or more metals of the iron group in conjunction with a difficultly reducible oxide, as a major ingredient, by adding to the catalyst mixture a small amount of a substance which will react with the difficultly reducible oxide, at a temperature above for example that usual for the production of hydrogen or gases rich in hydrogen by the methane-steam reaction, usually at about 820° Centigrade, to form a compound having a melting point above the melting point at which it is desired to conduct the methane-steam reaction and heating the mixture to the temperature at which the added substance and the oxide can react. If the difficultly reducible oxide associated with the metal of the iron group is of acidic nature, the added substance is preferably a basic oxide such as magnesia or lime, or barium oxide. If, on the other hand, the difficultly reducible oxide associated with the metal of the iron group is of basic nature.

the substance added to impart strength is preferably an acidic oxide such as alumina, boric acid, chromium oxide, molybdic acid, tungstic acid, etc. Where the difficultly reducible oxide is amphoteric, the added substance should preferably be of acidic nature, such as boric acid or phosphoric acid. In some instances the substance added may be a salt of fluorine, a silicate, or a hydrophosphate which is capable of reacting with the oxide associated with the metal of the iron group to form a high melting double salt.

In the preparation of catalysts for the methane steam reaction, for example, a difficultly reducible oxide is impregnated with an aqueous solution of a nickel salt, usually nickel nitrate, the mixture is roasted to dryness at a sufficiently high temperature to convert the nickel nitrate into nickel oxide and the mixture is then reduced at an elevated temperature by hydrogen so as to convert the nickel oxide to metallic nickel. To obtain a more intimate mixture of the nickel and the difficultly reducible oxide, solutions of salts of both may be mixed and the mixed hydroxides of both precipitated by the addition of ammonia or any other suitable precipitating agent. In such case the further treatment of the catalyst mixture is the same as mentioned above. In any case, in the methods normally employed for the production of these catalysts the roasting and reducing steps are carried out at temperatures usually not in excess of 600° Centigrade.

According to the process of the present invention the substance which is to be added to the metal oxide associated with the nickel may be added at any stage of the process prior to the final heating step. For example, it may be added during the initial mixing step or prior to or after the roasting step. Addition during the initial mixing step in the wet state is the preferred procedure. If desired, the catalyst material is subjected to a reducing treatment. Subsequently a high temperature heating step to a temperature substantially above the temperature at which the methane-steam reaction is to be conducted is carried out. This high temperature heating step is essential because the substance employed, according to the present invention, to increase the strength of the catalyst does not produce the desired effect at the temperatures usually employed for the methane-steam reaction.

The catalytic reactions in which the catalysts obtainable according to our invention exhibit their greatest utility are, as stated before, those in which the reaction temperature is upwards of 480° Centigrade. Among these may be mentioned the reaction between steam and hydrocarbons for the production of hydrogen, the cracking of hydrocarbons for the production of olefines, diolefines and acetylene, the dehydrogenation of hydrocarbons, the polymerisation of unsaturated normally gaseous hydrocarbons to aromatics, the destructive hydrogenation of distillable carbonaceous materials in the upper end of the operative temperature range of 300° Centigrade to 700° Centigrade, the synthesis of methanol, the reduction of oxides of carbon with or without pressure to produce liquid hydrocarbons, said reduction being carried out, if desired, at temperatures below 480° Centigrade, for example, at 180° to 210° Centigrade, and similar reactions.

In any of these reactions, the catalysts which have been found to exhibit the greatest activity contain one or more of the acid or basic substances or both employed according to the present invention. For example, for the methane-steam reaction catalysts composed of a metal of the iron group, usually nickel, and one or more of the oxides of aluminium, magnesium, chromium, tungsten, silicon, and uranium or a clay containing oxides of both a basic and acid character have been found satisfactory. For the catalytic dehydrogenation of hydrocarbons, catalysts containing oxides of metals of group 6 of the periodic system, phosphates and difficultly reducible oxides of metals of the fourth group of the periodic system have been employed. For destructive hydrogenation and for the methanol-synthesis, catalysts containing a large variety of difficultly reducible oxides of both basic and acid character have been proposed. For the reduction of oxides of carbon, catalysts comprising cobalt or other metals of the iron group as essential ingredients may be advantageously employed.

Where the catalyst mixture, as such, contains substances of acid and basic character in large amounts its strength can, of course, be improved by heating to the necessary temperature to cause these substances to react without the addition of any other substance. Sometimes, it may be practically impossible to control the heating step in such a case, however, so as to avoid a decrease in activity of the catalyst due to a too extensive reaction of the reaction components. This is especially true, where, as in the case of many common dehydrogenation catalysts, the acidic reactive component is the catalytically effective ingredient and is present in a relatively small amount. In such cases it is preferable, according to the present invention, to add to the catalytic mixture a small amount of a substance which has a greater affinity for either the acidic or basic component of the catalyst than does the other component of the catalyst. For example, in a catalyst composed of a small amount of chromic oxide and a large amount of alumina the strengthening should be effected by the addition of a few percent. of boric acid followed by the heating step, rather than by heating the catalyst itself without any addition.

Where the catalyst initially contains only a large amount of a substance of basic character, a small amount of an acid substance should be added before the heating step. Where the catalyst initially contains only a large amount of a substance of acid character, a small amount of a basic substance is added prior to the heating step. In cases where the catalyst contains a large amount of an amphoteric oxide, the added minor component is preferably acidic. For example, alumina may be combined either with phosphoric or with boric acid. Where the catalyst initially contains neither, or contains substances of either or both types which will not react with another substance to form a compound of the required high melting point, both types of substances must be added in small amounts.

The reactions by which the high melting compound contemplated by the present invention is produced ordinarily require the employment of temperatures upwards of 870° Centigrade. Since the present invention finds its greatest field of application in the production of pilled or tabletted catalysts in which it is impossible to employ materials of high mechanical strength, such as pumice, etc., the process of the present invention usually comprises both a roasting and a reducing step and in addition a moulding step and a high-temperature strength-increasing heating step. Of course, the roasting step may be omitted but it is preferably included prior to the moulding step so as to eliminate any water, if this is present, and decomposition gases, such as NO_2, during the heating of the moulded catalyst. The reducing step is usually conducted after the high temperature heating step. Furthermore, the high temperature heating step may be conducted in an inert or reducing atmosphere where the catalytically active ingredient is one which loses activity when heated to a high temperature in the presence of air.

It may be desirable to store the catalyst in an inert atmosphere, for example nitrogen, in order to avoid its activity being deteriorated in contact with air.

An especially active catalyst previously suggested for the methane-steam reaction is a catalyst composed of nickel and magnesia. This catalyst preferably contains a large amount of magnesia and nickel, and catalytic compositions containing 25 per cent. nickel and 75 per cent. magnesia are preferred. This catalyst, however, has been found to be particularly fragile at preferred operating conditions.

My foreign correspondents have found that this nickel magnesia catalyst can be rendered eminently satisfactory from the point of view of mechanical strength by being subjected to the strength improving process according to the present invention. The inorganic compound added to this mixed catalyst for the purpose of impoving strength is preferably one which has a melting point below about 820° Centigrade, in order to secure intimate mixing and rapid reaction between the added component and the magnesia. Examples of compounds which may be added to the nickel magnesia catalyst, as well as to other catalysts treated according to the present invention, are the acids and salts of fluorine and acids, oxides and salts of silicon, tin, germanium, bismuth, aluminium, lead, boron, cobalt, tungsten, phosphorus, chromium, molybdenum, manganese, and the like, such as sodium fluoride, silica, sodium silicate, alumina, boric acid, chromium oxide, cobalt oxide, molybdic acid, tungstic acid, phosphoric acid, etc. Weakly acidic compounds, such as boric acid and tungstic acid, are preferred.

Such compounds should be added in small amounts varying between 1/2 per cent. and 10 per cent. and preferably not in excess of 5 per cent. of the total catalyst mixture. My foreign correspondents have found that such minor amounts of the added substance are sufficient to impart the desired strength to the catalyst without impairing its activity, whereas when amounts substantially in excess of 10 per cent. are employed, the strength of the resulting catalyst is not appreciably greater, but its activity may be considerably less due to the fact that an extensive reaction between the added substance and the difficultly reducible oxide may cause a coating to form over some of the catalytically effective surface.

In the preferred form of performing of the present invention the catalyst is employed in pilled or tabletted form.

Graphite is a highly advantageous lubricant for the formation of pilled or tabletted catalysts. Due to the fact that graphite does not decompose at elevated temperatures, the heating of large pills or tablets can be conducted without the setting up of internal pressure in the pills or tablets. Consequently crumbling of the catalyst is entirely eliminated. Moreover by the employment of graphite as a lubricant the pilling or tabletting operation proceeds more smoothly and without any sticking of the pills or tablets in the pilling or tabletting machine. In addition it has been found that pilled or tabletted catalysts of all sizes are stronger when prepared with graphite as a lubricant than when prepared with any other lubricant previously proposed.

It is also possible in accordance with the present invention, to employ a lubricant which is combustible and is completely removed from the catalyst pills or tablets on heating to a temperature above about 820° Centigrade in air. Examples of such lubricants are the fatty acids, such as stearic or oleic acids and the mixed fatty acids obtained on limited oxidation of paraffin wax, for example, by blowing with air or with air containing oxides of nitrogen. Also high boiling viscous esters, such as the natural esters or the fatty esters including the natural oils, fats and waxes, and hydrocarbon lubricants such as the petroleum lubricating oils and waxes may be employed for this purpose. Since some of the catalysts according to the present invention, more particularly nickel catalysts, are sensitive to even slight traces of sulphur, it is preferable in such a case that the lubricants used with such catalysts be substantially free from sulphur.

The following Examples will further illustrate how the present invention may be carried out in practice but it should be understood that the invention is not limited to these Examples. The percentages are by weight unless otherwise stated.

EXAMPLE 1.

1455 parts by weight of nickel nitrate hexahydrates were dissolved in 500 parts of water, to which 22 parts of boric acid were added. 750 parts of magnesium oxide were then slowly added to the solution, with stirring, and the resulting paste was dried and heated at about 455°—475° Centigrade to convert the nitrates to oxides and to drive off oxides of nitrogen. The heated powder was passed through a 10 mesh screen and was then formed into a dense mass by compression under high pressure. This is suitably done in a tablet machine, using pressures of the order of 700 kilograms per square centimetre or higher. The tablets first formed may be made even stronger by being crushed to about 10 mesh and then again formed into tablets. The tablets resulting from this double operation are then heated to a temperature of 920° to 1090° Centigrade or higher for about 36 hours. The nickel oxide in the tablets is then reduced to metallic nickel by passing hydrogen over them for about six hours at the same or any desired lower temperatures. The resulting tablets are highly active catalysts for the production of hydrogen by the reaction of methane and steam, a gas containing 0.9 per cent. of methane being obtained on passing 250 volumes of methane per hour and excess steam over the tablets in an externally heated reaction tube maintained at 880° Centigrade.

The strength of the tablets thus prepared is much greater than that of tablets prepared in the same manner but without the addition of the boric acid. A comparison of the minimum pressure required to crush the tablets, with and without the addition of boric acid, is given in the following table:

Strength of Tablets
Kilograms per Square Centimetre

	Before Heating	After Heating
Tablets with 2 per cent. Boric Acid	71,4	295
Tablets without Boric Acid	49	132

EXAMPLE 2.

In order to demonstrate the manner in which catalysts employed according to the present invention are superior in stability to catalysts previously employed, tests were made on a nickel magnesia catalyst of the type described in the first Example containing different strength increasing additions. The strength of these catalysts was measured before heating, after heating for several hours at 920° Centigrade and after use in the methane steam reaction for a given period at a temperature between 810° Centigrade and 920° Centigrade. The catalysts were all employed as pills of the same size and shape. The crushing force was measured as kilograms per pill. The following results were obtained:

Catalyst	Before Heating	After Heating	After Use
Ni—MgO	11.32	9.98	7.27
Ni—Mgo+2 per cent. H_3BO_3	10.04	15.33	16.30
Ni—MgO+5 per cent. NaF	9.07	19.04	34.84
Ni—MgO+4 per cent. H_3PO_4	9.07	14.04	17.22

Example 3.

The nickel magnesia catalyst of the preceding Example when heated at 1150° Centigrade for 20 hours had a strength of 6.81 kilograms per pill. Two per cent. of boric acid added to the pills in the manner described increased the strength after the same heating step to 43.90 kilograms per pill. Ten per cent. of boric acid increased the strength to 37.18 kilograms per pill. Two per cent. of cobalt oxide increased the strength to 25.81 kilograms per pill. One-half per cent. of sodium fluoride increased the strength to 27.20 kilograms per pill. Two per cent. of sodium fluoride increased the strength to 33.90 kilograms per pill. Four per cent. of phosphoric acid increased the strength to 17.44 kilograms per pill.

Example 4.

In order to determine the effect of time of heating and temperature of heating on the strength of the catalyst produced, a nickel magnesia catalyst of the composition set forth in Example I containing 2 per cent. of boric acid was heated at successively higher temperatures for 20 to 23 hours and the strength of the pills after each heating step was measured. The results were as follows:

Temperature	Initial Strength	After Heating
870° C.	71.4	151.2
980° C.	71.4	286.7
1090° C.	71.4	388.0

In this table strength is given as kilograms per square centimetre.

The same catalyst was heated for different periods at two different temperatures. The results were as follows.

Hours	980° Centigrade	1090° Centigrade
12—14	130	255
20—22	210.5	357

Example 5.

A catalyst mixture composed of 4 per cent. by weight of chromium oxide, and 96 per cent. by weight of alumina, obtained by saturating alumina with the required amount of a solution of chromium nitrate and roasting at about 176° Centigrade, is mixed with 1 per cent. of graphite and 2 per cent. of boric acid and compressed into pills. The pills, when heated for 20 hours at 980° Centigrade had a strength of 1260 kilograms/square centimetre. Should the pills acquire a pink color in this step they suffer a substantial loss in catalytic activity. In order to prevent the occurrence of the conversion to which the pink coloration is due, the heating step, when temperatures upwards of 980° Centigrade are employed, should be conducted in an atmosphere of hydrogen, nitrogen, methane, or other reducing or inert gas. This catalyst exhibits satisfactory activity in the dehydrogenation of hydrocarbons at a temperature of about 540° Centigrade.

Example 6.

A catalyst mixture composed of 1 gram molecular weight of chromic oxide and 150 grams of magnesia has added to it 1 per cent. of graphite and 2 per cent. of boric acid and is pilled. The pills, upon being heated for 20 hours at 810° Centigrade show a resistance to pressure of 965 kilograms per square centimetre. When heated for 20 hours at 920° Centigrade the pills show a resistance to pressure of 1366 kilograms per square centimetre. When heated at 1090° Centigrade for 20 hours the pills show a resistance to pressure of 3780 kilograms per square centimetre. When the content of magnesia in the catalyst is doubled and the pills are heated at 910° Centigrade for 20 hours the resistance to pressure is 2190 kilograms per square centimetre. This catalyst is also suitable for use in the dehydrogenation of hydrocarbons when care is taken to avoid a pink coloration during the heating step.

Example 7.

1455 parts by weight of nickel nitrate hexahydrate were dissolved in 500 parts of water. 750 parts of magnesium oxide were then slowly added to the solution with stirring and the resulting paste was dried and heated at about 455—475° Centigrade to convert the nitrates to oxides and to drive off the oxides of nitrogen. The heated powder was passed through a 10 mesh screen and was then formed into a dense mass by compression, using pressures of the order of 700 kilograms per square centimetre in a tablet machine. The tablets were in the form of right cylinders, 0.489 centimetre in diameter and 0.489 centimetre in height. The tablets first formed were crushed to about 10 mesh and then again formed into tablets, thereby removing occluded air and improving their strength. The second tablets were then heated in air to a temperature of 920° Centigrade to 1090° Centigrade for about 36 hours. The nickel oxide in the heated tablets was then reduced to metallic nickel by passing hydrogen over them at the same temperature for about 6 hours.

The strength of the tablets, measured as the maximum load carried by the tablet, without crushing, when applied to diagonally opposite sides of the cylinder, was 10.9 kilograms.

Tablets were formed, heated, reduced and tested for strength, as in the first paragraph of the present Example, with the exception that 1 per cent. stearic acid was mixed thoroughly with the heated powder of nickel and magnesium oxides before the tabletting operation. The tabletting operation was, however, conducted much more smoothly.

The strength of the tablets thus prepared from a mixture containing stearic acid was 14.5 kilograms.

Tablets were formed as in the first paragraph of the present Example with the exception that 2 per cent. of boric acid was added to the nickel nitrate solution. The strength of the tablets thus prepared was 15.9 kilograms.

Tablets were prepared as in the first paragraph of the present Example with the exception that 1 per cent. of stearic acid and 2 per cent. of boric acid were added. The strength of the tablets thus prepared from a mixture containing both stearic acid and boric acid was 17.7 kilograms.

EXAMPLE 8.

1455 parts by weight of nickel nitrate hexahydrate were dissolved in 500 parts of water. 750 parts of magnesium oxide were then slowly added to the solution with stirring and the resulting paste was dried and heated at about 455—475° Centigrade to convert the nitrates to oxides and to drive off the oxides of nitrogen. The heated powder was passed through a 10 mesh screen and was then formed into a dense mass by compression, using pressures of the order of 700 kilograms per square centimetre in a tablet machine. The tablets were in the form of right cylinders, 0.489 centimetre in diameter and 0.489 centimetre in height. The tablets first formed were crushed to about 10 mesh and then again formed into tablets, thereby removing occluded air and improving their strength. The second tablets were then heated in air to a temperature of 1090° Centigrade for 24 hours. After use in the methane-steam reaction, these tablets showed a resistance to crushing of 56 to 84 kilograms per square centimetre.

EXAMPLE 9.

Two catalysts of the same composition of nickel and magnesia were prepared in the manner described in Example 8. In the first, before pilling, 2 per cent. of boric acid was incorporated and the catalytic pills were heated for 22 hours at 980° Centigrade. The pills so prepared, after being used in the methane-steam reaction, showed a resistance to crushing of 210 kilograms per square centimetre. During the pilling operation many of the pills crumbled and frequent interruption of the pilling operation was caused by sticking of the pills in the pilling machine.

In the second batch of catalyst 2 per cent. of boric acid and 1 per cent. of graphite were added prior to the pilling operation. The pilling operation proceeded without any interruption due to sticking and no crumbling of the pills occurred. This catalyst was heated in pill form for 22 hours at 980° Centigrade. After being used in the methane-steam reaction, under the same conditions and for the same period as in the previous example, these pills showed a resistance to crushing of 231 kilograms per square centimetre.

When the pills of this last batch were heated at 1090° Centigrade for 32 hours, they showed, after the same period of use in the methane-steam reaction, a resistance to crushing of 394 kilograms per square centimetre.

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

1. A process for the production of a catalyst of high mechanical strength, adapted for reactions conducted at high temperatures, which comprises forming into pieces, by compression under high pressure of at least 500 atmospheres, a finely divided compounded material, comprising an effective catalytic substance and the melting point of which is substantially higher than the temperature in the subsequent heating or which forms

a substance of said melting point in the subsequent heating, and heating the pieces to a temperature of at least 850° C. thereby effecting a substantial increase of strength.

2. A process as claimed in Claim 1, in which the finely divided compounded material is a powder.

3. A process as claimed in Claim 1 and 2, in which the finely divided compounded material is a dry powder.

4. A process as claimed in any of Claims 1 to 3, which comprises crushing the pieces which have been heated to a temperature of at least 850° Centigrade, forming the resulting powder into pieces by compression under high pressure and again heating the pieces to a temperature of at least 850°.

5. In the process as claimed in any of Claims 1, 2 and 4, a preliminary treatment which comprises forming the finely divided compounded initial material in a moist condition into pieces under any suitable conditions of pressure, and heating the pieces to a temperature sufficiently high to dry said material.

6. A process as claimed in any of Claims 1 to 5, which comprises preparing the initial finely divided compounded material by mixing a compounded material comprising an effective catalytic substance with a substance capable of interacting with said material to form a compound having a melting point substantially higher than the temperature in the subsequent heating, heating the mixture to a temperature at least sufficient to cause said compound to be formed, and crushing the compound produced if said compound is not present in a sufficiently fine state of sub-division.

7. A process as claimed in any of Claims 1 to 6, in which the material comprising an effective catalytic substance is a difficultly reducible acidic or amphoteric metal oxide.

8. A process as claimed in any of Claims 1 to 7, in which a difficultly reducible inorganic acid or amphoteric metal oxide is mixed with a small amount of a basic oxide, capable of reacting with said difficultly reducible acidic or amphoteric metal oxide to form a compound having a melting point substantially higher than the temperature of the subsequent heating.

9. A process as claimed in any of Claims 1 to 6, in which the material comprising an effective catalytic substance is a basic metal oxide or a metal compound reacting like a basic metal oxide in the subsequent heating.

10. A process as claimed in any of Claims 1 to 6 and 9, in which a basic metal oxide or a metal compound reacting like a basic metal oxide in the subsequent heating is mixed with a small amount of an inorganic acid, or an acid metal oxide or an amphoteric metal oxide, capable of reacting with said basic metal oxide to form a compound having a melting point substantially higher than the temperature in the subsequent heating.

11. A process as claimed in any of Claims 1 to 10, in which an oxide of the metal of groups 3 to 8 of the periodic system of the elements is caused to react with an oxide of an alkali metal or an alkaline earth metal, including magnesium, or another compound of such alkaline metals, to form a substance having a melting point substantially higher than 850° Centigrade.

12. A process as claimed in any of Claims 1 to 7, in which the compounded material comprising an effective catalytic substance is capable, on heating, of forming a double compound, the melting point of which is substantially higher than the temperature in the subsequent heating.

13. A process as claimed in any of Claims 1 to 12, which comprises preparing the initial finely divided compounded material by causing a finely divided compounded material, comprising a metal of the iron group, or a compound of said metals, and one or more of the oxides of aluminium, magnesium, chromium, tungsten, silicon and uranium and a small amount of boric or phosphoric acid to interact by heating, and crushing the resulting mass.

14. A process as claimed in Claim 12, in which the pieces are subjected to a heating treatment in the presence of reducing gases, after the heat treatment to at least 850° Centigrade, to reduce to a metallic state the metal of the iron group.

15. A process for the production of hydrogen by the interaction of oxides of carbon and/or of gaseous hydrocarbons with steam, in which a catalyst according to Claims 13 or 14 is employed.

16. The application of a catalyst prepared in accordance with any of Claims 1 to 14 from a mixture of at least one of the oxides of metals of group 6 of the periodic system, with a phosphate and/or a difficultly reducible oxide of a metal group 4 of the periodic system in the catalytic dehydrogenation of hydrocarbons.

17. The application of a catalyst prepared in accordance with any of Claims 1 to 14 from the material comprising a metal of groups 5 or 6 of the periodic system of the elements, or a compound of such a metal in the destructive hydro-

genation of carbonaceous materials.

18. The application of a catalyst prepared in accordance with any of Claims 1 to 14 from material comprising a metal of groups 5, 6 or 8 of the periodic system of the elements, or a compound of such a metal, in the production of methanol and/or liquid hydrocarbons from oxides of carbon and hydrogen.

19. A process as claimed in any of the preceding claims in which the strength of the catalyst has been substantially increased by heating at a temperature of at least 920° C.

20. The process for the production of catalysts substantially as described in the foregoing Examples.

21. Catalysts when produced according to the processes claimed in Claims 1 to 14 and 19.

Dated this 27th day of January, 1937.
W. P. THOMPSON & CO.,
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Chartered Patent Agents.

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