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COMPLETE SPECIFICATION.

Improvements relating to the Production of Catalysts, more particularly for the Dehydrogenation of Hydrocarbons.

We, STANDARD OIL DEVELOPMENT COMPANY, a corporation duly organised and existing under the laws of the State of Delaware, United States of America, having offices at Linden, New Jersey, and 100, West 10th Street, Wilmington, Delaware, both in the United States of America, 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:—

In catalytic processes in which temperatures upwards of 900° F., and up to about 2000° F., 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 the catalysts which have been found effective have been found 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 great 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 readily peels off after a relatively short time of usage.

We have found that catalysts of the active type of great mechanical strength can be produced without the employment of solid carriers by combining with the catalyst two or more substances capable of reacting with each other to form a solid supporting compound of high mechanical strength or of forming solid solutions, the compound or solid solution having a melting point considerably above the temperature at which the reaction in which the catalyst is to be employed is carried out, preferably above 2000° F. The amounts of the reacting substances used are such as to produce not more than 10% of supporting compound and the mixture is heated to a sufficiently high temperature above 1600° F. and above the temperature of the reaction in which it is to be employed and for a sufficiently long time to effect a substantial increase in strength, but insufficient to cause substantial melting, presumably by causing the high melting compound to be formed in sufficient amounts to exercise a binding effect.

It has already been proposed in British Patent No. 272,555 to prepare oxygenated carbon compounds by passing a carbon compound in the form of a gas or vapour at suitable temperature and pressure over a catalyst containing chromium in the tervalent form, the catalyst being prepared by subjecting mixtures or compounds containing hexavalent chromium and one or more of the group of metals zinc, copper, cadmium, magnesium, manganese, silver or iron, to treatment at a temperature above 600° C.

It has also been proposed in British Patent No. 359,620 to employ mixtures of solid oxides substantially free from those oxidisable metals (or compounds thereof) the compounds of which are reducible under the working conditions to the metal or to compounds of a lower oxidation stage (such as iron, nickel or cobalt) as catalysts in the thermal splitting of hydrocarbons. For example, mixtures of two or more of the oxides of aluminium, boron, zirconium, silicon, the alkaline earth metals and other metals, the solid oxides of which are not reducible under the working conditions may be employed.

In the process according to our invention the substances added to the catalyst must be employed only in such amounts that the compound or solid solution formed by their reaction constitutes a minor component of the catalyst, never more than 10% thereof. The reason for this is that too expensive 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, since the raw material used is frequently a mixture, and it is usually present as a major component thereof, thereby necessitating the addition of only a small amount of the other reactive component in order to effectuate the process of 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 chemically 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 1500° F. 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 added, however, have melting points higher than 1500° F. Acid substances according to the present invention are those substances or their compounds which give an acid reaction in water solution or which in a chemical compound constitute or occur in the anion. Basic substances according to the present invention are those which in water solution give an alkaline reaction or, in a chemical compound, constitute or occur in 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, 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 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 900° F. Among these may be mentioned the reaction between the steam and hydrocarbons for the production of hydrogen, the cracking of hydrocarbons for the production of olefines, diolefines and acetylenes, the dehydrogenation of hydrocarbons, the polymerization of unsaturated normally gaseous hydrocarbons to aromatic hydrocarbons, the destructive hydrogenation of distillable carbonaceous materials in the upper end of the operative temperature range of 300° C. to 700° C., the synthesis of methanol, and similar reactions.

In any of these reactions, the catalysts which have previously 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 alumina, 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 Group 4 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.

Our invention is particularly directed to the dehydrogenation of hydrocarbons. Hydrocarbons are ordinarily dehydrogenated by being conducted through an elongated upright reaction space which is packed with a catalyst. Due to the fact that the reaction temperature is relatively high, ordinarily of the order of 1000° F. and upwards, and the stream of reaction gases is quite rapid, together with the fact that the catalyst employed is of comparatively heavy nature, the portion of the catalyst in the lower part of the tower rapidly disintegrates and becomes unsuitable for use, both by reason of loss of effective surface and by reason of the fact that the fine material formed by disintegration becomes a serious obstruction to the free passage of the gaseous reaction material. In addition such catalysts usually become fouled by deposition of carbon thereon and must be periodically reactivated. This reactivation is usually effected by burning off the carbon. In this step the catalyst is subjected to even more destructive conditions than obtained in the dehydrogenation step itself, and suffers considerable deterioration.

We have now found that dehydrogenation can be conducted for interminable periods without interruptions due to disintegration of the catalysts by being carried out in the presence of a catalyst which has been prepared by including in its initial composition, in addition to the active catalytic ingredient, at least two substances, not having an adverse action in the dehydrogenation process, capable of reacting with each other at a temperature substantially higher than the temperature employed in the dehydrogenation process to form a compound or of producing a solid solution, the compound or solid solution having a fusion temperature considerably above the temperature of the dehydrogenation reaction, and heating the mixture for a substantial period at the reaction temperature of said two substances for a length of time sufficient to impart to the catalyst the desired strength. The temperature to which the catalyst composition must be heated in order to acquire strength is at least 1600° F.

Where the effective catalyst consists of a mixture of substances of acid and basic character in large amounts its strength could be improved by heating to the necessary temperature to cause these substances to react without the addition of any other substance. It is 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 reactive 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 necessary, 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 so that in such cases one component of the catalyst takes part in the formation of the supporting compound. 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.

Where the catalyst initially contains a large amount of a substance of basic character, and a small amount of a second substance which may be basic, acid or inert, a small amount of an acid substance should be added before the heating step. Where the catalyst initially contains a large amount of a substance of acid character, and a small amount of a second substance, which may be basic, acid or inert, 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, and a small amount of a second substance, which may be basic, acid or inert, 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.

It has already been proposed to produce catalysts for the methane-steam reaction by saturating a difficultly reducible oxide with nickel nitrate, drying the mixture, roasting it to decompose nickel nitrate to nickel oxide and reducing it to convert nickel oxide to metallic nickel. An alternative procedure is to mix a solution of a nickel salt with a solution of a salt of a metal capable of forming a difficultly reducible oxide simultaneously precipitating the hydroxides of the two metals, drying the mixture and reducing at an elevated temperature to produce a metallic nickel in the mixture. In either case neither the roasting nor reducing step is a heating step of the type contemplated for the strengthening of the catalyst according to the present invention. The roasting and reducing steps are ordinarily carried out at a temperature not substantially in excess of 600° C. The reactions by which the high melting compound contemplated by the present invention is produced do not ordinarily occur at such temperatures but require the employment of temperatures of at least 1600° F.

Since the present invention finds its greatest field of application in the production of pilled 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 the roasting and the reducing steps of the conventional method and in addition a molding 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 molding step so as to eliminate water and decomposition gases, such as NO_2, during the heating of the molded 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 has also been proposed for the methane-steam reaction to produce a catalyst by reacting a nickel salt with a metal acid to form a nickel metallate. Lest this procedure be confused with the procedure according to the present invention, it is pointed out that this reaction is ordinarily carried out in water solution at a relatively low temperature and that the nickel metallate formed is and must be decomposed during the roasting step since the nickel must be present in the metallic state in order to be effective for this reaction.

It is not precisely known what change occurs during the heating step to account for the increase in strength. It may be that one reaction component melts at the temperature employed and combines with the other component thereby setting up a bond between the particles of the catalyst. On the other hand, the temperature may be sufficiently high that the compound formed by the reaction of the two components may fuse and form a physical bond between the other components of the catalyst although there is never complete fusion of the catalyst as a whole. Again, in view of the fact that the components in many instances melt at temperatures much higher than the treating temperature, it may be that the components react in the dry state and in this way exert a binding effect.

Whatever be the explanation, it is a fact that where the two reaction components are present and the mixture is heated to a temperature over 1600° F. and usually in excess of 1700° F. but not necessarily in excess of the melting point of the compound which may be formed by the reaction between the said components, for a sufficient length of time, the strength of the catalyst is materially increased.

The best results are obtained when the final heating step is conducted at a temperature of about 2000° F. for a period ranging from ten to twenty hours. In cases where this high temperature reduces the activity of one or more of the catalytic components, the heating step may be conducted for a longer period at a lower temperature above 1600° F. In general the time of the heating step, for a given increase in strength, may be said to vary inversely with the temperature.

In order that the improved results of the present invention may be obtained it is essential that the catalyst composition, prior to the high temperature step, contain a catalytically active ingredient in a minor proportion, an acidic or basic substance, acting as a carrier, in a major proportion, and a small amount of an inorganic substance capable of reacting with the major component to form a high melting compound. Moreover, where the effective ingredient is itself capable of reacting with the major component the inorganic substance must be one which has a greater affinity for the major component than does the catalytically effective ingredient.

Our invention will be more completely understood from the following specific examples which are submitted purely for illustrative purposes and not for the purpose of defining the scope of our invention:—

EXAMPLE I.

A catalyst mixture composed of 4% of chromic oxide, by weight, and 96%, by weight, of alumina, obtained by saturating alumina with the required amount of a solution of chromium nitrate and heating at about 350° F. is mixed with 1% by weight of graphite and 2% by weight of boric acid and compressed into pills. The pills had an initial strength of 240 lbs./sq. in. Upon being heated for twenty hours at 1500° F. the pills had a strength of 103 lbs./sq. in. The same pills, when heated for twenty hours at 1700° F. had a strength of 180 lbs./sq. in.

In several runs, butane was passed over these pills at a temperature varying between 900° F. and 1100° F. In these runs the butane was converted into unsaturates, mainly butylenes, in amounts varying between 20% and 50% of the initial material. No indication of disintegration of the catalyst, as for example the formation of fines, was noticed.

The same catalyst when prepared without the use of boric acid showed an initial strength after pilling of 310 lbs./sq. in., but after being subjected to 1800° F. for twenty hours, crumbled readily between the fingers.

The same catalyst, without the preliminary heating at 350° F. and without the use of boric acid, formed satisfactory pills, having an initial strength of 206 lbs./sq. in., but on heating in 1700° F. for twenty hours exhibited a strength of only 105 lbs./sq. in. and gave evidence of disintegration when used for dehydrogenation.

Catalysts comparable in durability and activity to that obtained by use of boric acid were produced by the use, instead of

2% of boric acid, of 3% by weight of H_3PO_4 and 1% by weight NaF, respectively.

Example II.

A catalyst mixture composed of one gram molecular weight of chromic oxide and 150 grams of magnesia, together with 1% by weight of graphite and 2% by weight of boric acid, was pilled under high pressure and, after being heated for twenty hours at 1700° F., had a resistance to crushing of 2670 lbs./sq. in. On being heated for twenty hours at 2000° F. the pills had a resistance to crushing of 5400 lbs./sq. in.

In all cases, this catalyst, on use in the dehydrogenation of hydrocarbons, showed no tendency to disintegrate.

In some cases the catalyst suffers a loss in activity by oxidation during the heating step above 1800° F. This may be avoided by conducting the heating step in a reducing atmosphere or in an inert atmosphere, or by following the heating step with a treatment with hydrogen or other reducing gas at the same temperature.

Example III.

1455 parts by weight of nickel nitrate hexahydrate were dissolved in 500 parts of water, to which 22 parts by weight of boric acid were added. 750 parts by weight of magnesium oxide were then slowly added to the solution, with stirring, and the resulting paste was dried and heated at about 850—900° F. to convert the nitrate 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 10000 pounds per square inch 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 1700 to 2000° F. 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% 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 1525° F.

The strength of the tablets thus prepared is much greater than 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 Pounds per Square Inch.	
	Before Heating.	After Heating.
Tablets with 2% by weight Boric Acid	1020	4150
Tablets without Boric Acid	700	1890

Example IV.

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 third example containing different strength increasing additions. The strength of these catalysts was measured before heating, after heating for several hours at 1700° F. and after use in the methane steam reaction for a given period at a temperature between 1500° and 1700° F. The catalysts were all employed as pills of the same size and shape. The crushing force was measured as pounds per pill. The results obtained are given in the following table, data for the Ni-MgO catalyst being included for comparison, although it is not intended to use this catalyst:—

Catalyst.	Before Heating.	After Heating.	After Use.
Ni-MgO	25	22	16
Ni-MgO + 2% by weight H_3BO_3	23	35	36
Ni-MgO + 5% by weight NaF	20	42	77
Ni-MgO + 4% by weight H_3PO_4	20	31	38

EXAMPLE V.

The nickel magnesia catalyst of the preceding example when heated at 2100° F. for 20 hours had a strength of 15 lbs. per pill. Two per cent. by weight of boric acid added to the pills in the manner described increased the strength after the same heating step to 97 lbs. per pill. Ten per cent. of by weight of boric acid increased the strength to 32 lbs. per pill. Two per cent. of cobalt oxide increased the strength to 57 lbs. per pill, by the formation of a solid solution of cobalt oxide and magnesia. One half per cent. by weight of sodium fluoride increased the strength to 60 lbs. per pill. Two per cent. by weight of sodium fluoride increased the strength to 77 lbs. per pill. Four per cent. by weight of phosphoric acid increased the strength to 38 lbs. per pill.

EXAMPLE VI.

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 III containing 2% by weight of boric acid was heated at successively higher temperatures for 20 to 22 hours and the strength of the pills after each heating step was measured. The results were as follows:—

Temperature.	Initial Strength	After Heating.
1600° F.	1020	2160
1800° F.	1020	4100
2000° F.	1020	5450

In this table strength is given as pounds per square inch.

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

Hours	1800° F.	2000° F.
12—14	1860	3650
20—22	3100	5100

We are aware that it has previously been proposed to use, in the production of methanol, and other carbon compounds, catalysts prepared by the fusion of mixtures which contain cupric oxide and manganese dioxide, together with one or more of the oxides of magnesium, aluminium, chromium, zirconium, vanadium, titanium, thorium, silicon and cerium.

Catalysts prepared by melting together magnesium oxide, aluminium oxide and ferroso-ferric oxide have also been employed in the catalytic decomposition of ammonia.

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 what we claim is:—

1. A process for the production of a catalyst of high mechanical strength adapted for reactions conducted at a temperature in excess of at least about 900° F. which comprises mixing with an effective catalytic substance at least two substances, one as a major ingredient and the other as a minor ingredient, capable of reacting with each other to the exclusion of the effective catalytic substance to form a compound or of forming a solid solution, the compound or solid solution having a melting point substantially higher than the temperature of the reaction in which the catalyst is to be employed, and heating the catalytic mixture at a sufficiently high temperature above 1600° F. and for a length of time sufficient to effect a substantial increase in the mechanical strength thereof, but insufficient to cause substantial melting, the amount of compound or solid solution formed being not greater than 10% of the total catalyst mixture.

2. A process for the production of a catalyst according to the preceding Claim in which the two substances mixed with the effective catalytic substance are respectively an acid substance and a basic substance, at least one of these being a difficultly reducible metal oxide.

3. A process according to Claims 1 and 2, wherein the effective catalytic substance is present as a minor ingredient.

4. A process according to Claim 2, wherein there is mixed with the effective catalyst a difficultly reducible acidic or amphoteric metallic oxide as major ingredient, and a basic oxide as minor constituent.

5. A process according to any of the preceding Claims, wherein the catalyst mixture is prepared in tablet form, before being heated at a temperature above 1600° F.

6. A process according to Claim 2, wherein there is mixed with the effective catalyst a difficultly reducible basic oxide as major constituent and an inorganic acid, acidic oxide or amphoteric oxide as minor constituent.

7. Process according to Claim 6, wherein the difficultly reducible basic oxide is magnesium oxide or aluminium oxide and the inorganic acid is boric acid or phosphoric acid.

8. Process according to Claim 7, in which the effective catalytic substance is chromic oxide, nickel oxide or iron oxide.

9. A process for the dehydrogenation of

hydrocarbons which comprises passing a hydrocarbon at a temperature of at least 900° F. over a catalyst, whenever prepared by the processes claimed in any of the preceding Claims.

10. A process according to Claim 7, wherein the catalyst is in the form of pills, packed in an elongated upright reaction zone, and comprises an oxide of a metal of group six of the periodic system and an oxide of an alkaline earth metal and an inorganic substance capable of reacting with the alkaline earth oxide at the temperature at which the mixture is heated.

11. A process according to Claim 9, wherein the catalyst is in the form of pills, packed in an elongated upright reaction zone, and comprises an oxide of a metal of group six of the periodic system, alumina, a small amount of a lubricant and a small amount of an inorganic substance capable of reacting with alumina at the temperature at which the mixture is heated.

12. A process according to the preceding Claims, wherein the substance added for reaction with alumina is boric acid.

13. Processes for preparing catalysts substantially as described in the Examples I to VI.

14. Processes for dehydrogenating hydrocarbons substantially as described in Examples I and II.

15. Processes for reacting methane with steam substantially as described in Examples III and IV.

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