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COMPLETE SPECIFICATION

Hydrocracking Catalyst

We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of No. 30 Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a catalyst for the conversion of hydrocarbons. More specifically the invention is concerned with a hydrocarbon conversion catalyst which may be used for hydrocracking hydrocarbons and to a process for preparing such a catalyst.

Destructive hydrogenation, which may also be referred to as "hydrocracking", as distinguished from the simple addition of hydrogen to unsaturated bonds between hydrocarbons, involves definite changes in structure, and may be designated as cracking under hydrogenation conditions so that the lower boiling products of the cracking reactions are substantially more saturated than when hydrogen or materials supplying hydrogen are not present. Destructive hydrogenation processes are most commonly employed on coals or heavy residual or distillate oils for the production of substantial yields of low boiling saturated products and to some extent to produce intermediates which are utilizable as domestic fuels, and still heavier cuts which find uses and are suitable as lubricants. These destructive hydrogenation, or hydrocracking, processes may be operated either on a strictly thermal basis or in the presence of catalyst. A large number of materials have been employed as catalysts, for example, the metals of the iron group, including iron, nickel or cobalt, and the oxides and sulfides of chromium, molybdenum and tungsten representing the metals in the left-hand column of Group VI of the Periodic Table (Group VI A). In addition numerous mixed metal and metal oxide catalysts have also been tried, as well as less common metal salts.

The hydrocracking, or splitting of carbon to carbon bonds, is relatively important in treating cracked gasolines, particularly thermally cracked gasoline, either alone or in admixture with straight-run gasoline. Controlled or selective cracking is highly desirable because such cracking normally results in a product of improved anti-knock characteristics. In general, the lower molecular weight products possess higher octane numbers, and thus a final gasoline product of lower average molecular weight will usually have a higher octane rating. Furthermore, during the cracking reaction, isomerization or other molecular rearrangement occurs which also results in products having higher anti-knock characteristics. The selective cracking is of particular advantage when the charge stock contains components boiling above about 204° C. in order to convert these components to fractions boiling below about 204° C. Therefore, it is readily apparent that the selective cracking results not only in an improved quality product, but also in an increase in the quantity of the desired product.

However, the cracking must be selective and must not result in the decomposition of the normally liquid hydrocarbons substantially or completely into normally gaseous hydrocarbons. The desired selective cracking generally comprises the splitting of a higher boiling hydrocarbon molecule into two molecules both of which are normally liquid hydrocarbons. To a lesser extent it comprises the removal of methyl, ethyl and propyl groups which, in the presence of hydrogen, are converted to methane, ethane and propane. However, the removal of these radicals is minimized by controlling the catalyst composition and to some extent by controlling the reaction conditions. For example, in the presence of hydrogen, decane may be re-

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duced to two pentane molecules, heptane to hexane and nonane to octane or heptane. On the other hand, uncontrolled or non-selective cracking will result in the decomposition of normally liquid hydrocarbons into normally gaseous hydrocarbons as, for example, by the continued demethylation of normal heptane to produce seven methyl groups which, in the presence of hydrogen, are converted to methane.

Another important objection to non-selective or uncontrolled cracking is that this type of cracking will result in the more rapid formation of larger quantities of coke or carbonaceous material which deposits on the catalyst and decreases or destroys its activity to catalyze the desired reactions. This in turn results in shorter processing cycles or periods, with the necessity of more frequent regeneration of the catalyst by burning the carbonaceous product therefrom. Should the catalyst activity be destroyed, it may be necessary to shut down the unit to remove the old catalyst and replace it with new catalyst.

The present invention provides a process for preparing a hydrocracking catalyst which will permit a hydrocracking process to operate at the most economically attractive conditions whereby the maximum amount of hydrocarbons is selectively converted into desired products. In this process according to the invention a refractory solid support having ~~cracking~~ cracking activity and consisting essentially of silica and at least one oxide of the group of alumina, magnesia, zirconia and thoria is impregnated with a solution of at least one of the compounds of the metals of Groups VI A and VIII of the Periodic Table of Elements, said solution constituting the source of an active hydrogenating metal component in the final catalyst, the impregnated support is heated in an oxidizing atmosphere at a temperature substantially in the range of from 700 to 760° C. for a period of from 1 to 8 hours, and the thus oxidized composite is subjected to a reducing treatment with hydrogen at an elevated temperature.

The present invention further provides, as the product of the herein defined process of catalyst preparation, a hydrocracking catalyst which will fulfil all of the requirements of controlled or selective hydrocracking hereinabove set forth so that the optimum yields of the desired product may be obtained in the hydrocracking process.

A method for the regeneration of a catalyst of the kind provided by the present invention, after it has become deactivated during use in a hydrocracking operation, is described and claimed in our co-pending Application No. 5207/61 (Serial No. 917,470).

It has been discovered that the temperature at which a composite comprising a compound of at least one of the metals of Groups VI A and VIII of the Periodic Table of Elements on a solid support is calcined or oxidized is important in obtaining a catalyst which will operate at maximum efficiency in obtaining the desired hydrocracking product description. Thus, apart from the support, the catalyst comprises at least one metal, or oxide thereof, selected from the group consisting of chromium, molybdenum, tungsten, iron, cobalt, nickel, palladium, platinum, ruthenium, rhodium, osmium and iridium. The solid supports are materials which are effective as cracking catalysts, for example, naturally occurring aluminum silicates, particularly when acid treated, and synthetically produced composites of silica-alumina, silica-zirconia, silica-alumina-zirconia, silica-magnesia, silica-alumina-magnesia and silica-alumina-thoria. The preferred solid support comprises a synthetic composite of silica and alumina. A particularly preferred support consists of approximately 63% by weight of alumina and 37% by weight of silica and, as hereinafter more fully described and illustrated by way of example, such support is advantageously impregnated with an aqueous solution containing nickel nitrate in an amount which imparts to the final catalyst a platinum or palladium content of between 0.01 and 10% by weight.

The synthetically produced solid ~~support~~ supports may be made in any suitable manner, including separate, successive or co-precipitation methods. For example, alumina may be prepared by adding a reagent such as ammonium hydroxide or ammonium carbonate to a salt of aluminum such as aluminum chloride, aluminum nitrate or aluminum acetate, in an amount to form aluminum hydroxide, which upon drying is converted to alumina. A chloride of aluminum is generally preferred as the aluminum salt to be used, for convenience in subsequent washing and filtering procedures and also because it appears to give best results. After the alumina has been formed it is generally washed and filtered one or more times to remove soluble impurities, the filtration of the alumina being improved when the wash water contains a small amount of ammonium hydroxide.

Silica may be prepared in any suitable manner, for example by commingling water glass and a mineral acid under conditions to precipitate a silica hydrogel, which is washed with water containing a small amount of electrolyte to remove sodium ions. Oxides of magnesium, thorium and zirconium may be prepared by similar, well-known methods.

When it is desired to prepare the catalyst in the form of particles of uniform size and shape, this may readily be accomplished by grinding the partially dried oxide cake with a suitable lubricant such as stearic acid, rosin or graphite, and then forming the particles in any suitable pelleting or extrusion apparatus.

a nickel content of from 1 to 6% by weight or with an aqueous solution of a compound of platinum or palladium in an amount which imparts to the final catalyst

The preferred cracking components comprising silica-alumina and silica-alumina-zirconia are preferably manufactured by commingling an acid such as hydrochloric acid or sulfuric acid, with commercial water glass under conditions to precipitate silica, washing with acidulated water or otherwise to remove sodium ions, commingling with an aluminum salt such as aluminum chloride, aluminum sulfate, aluminum nitrate and/or zirconium salt, and either adding a basic precipitant such as ammonium hydroxide to precipitate alumina and/or zirconia, or forming the desired oxide or oxides by thermal decomposition of the salt as the case may permit. The silica-alumina-zirconia cracking component may be formed by adding the aluminum and/or zirconium salts together or separately. The other cracking components may be prepared in a similar manner, however, not necessarily with equivalent results. Spherically-shaped oxides or oxide-composites are also highly suitable. These may be prepared by known methods, usually involving passing droplets of colloidal solutions of the oxides into an oil bath under conditions causing setting of the materials to gel spheres, which are then aged, washed and dried. A typical method of preparing a silica-alumina cracking component is hereinafter illustrated in the first one of the examples, and the cracking component produced in this example represents a particularly preferred support for use in the catalyst of the present invention.

The component of the catalyst comprising the Group VI A and/or Group VIII metal is composited with the solid support generally in a total amount of from 0.01% to 20% by weight of the catalyst, calculated as metal. The particularly desirable metals include platinum, palladium, nickel and molybdenum, and they may be incorporated into the catalyst in any suitable manner. One such manner is to composite the metal component with the support having cracking activity by forming an aqueous solution of the halide of the metal such as platinum chloride, palladium chloride, nickel chloride, molybdenum chloride, chromium chloride, tungsten chloride, platinum bromide, palladium bromide, nickel bromide or molybdenum bromide, or of a nitrate, for example nickel nitrate, molybdenum nitrate, or ammonium molybdate, then further diluting the solution and adding the resultant diluted solution to the support having cracking activity in a steam drier. In an alternative method, separate aqueous solutions of the metal compound and ammonium hydroxide are added to give the resultant solution a pH between the range of from about 5 to about 10. This solution is then commingled with the other component of the catalyst. Other suitable forms in which the metals may be employed include colloidal solutions or suspensions of for example, the cyanide, hydroxide, or sulfide of the desired metal.

The concentration of the metal or metal oxide component selected from Groups VI A and VIII of the Periodic Table preferably will lie within the range of from 0.01% to 10% by weight of the final catalyst (calculated as the metal).

The resultant composite after all of the components of the catalyst are present therein is then dried for a period ranging from about 1 to about 8 hours or more in a steam drier and then oxidized in an oxidizing atmosphere such as air or other oxygen-containing gas at a temperature in the range of from 700° to 760° C. for a period of time ranging from about 1 to about 8 hours or more. The catalyst is then reduced for a period ranging from about one-half hour to about one hour at a temperature in the range of from 260° to 540° C. in the presence of hydrogen. It is also contemplated within the scope of this invention that the reduction of the catalyst prior to use thereof may be accomplished by reducing the catalyst in situ by means of a hydrogen purge at a temperature of about 315° C. after the catalyst has been placed in a hydrocracking reaction zone and before the material to be hydrocracked is introduced into this reaction zone.

As indicated above the catalysts which are formed according to the process of the present invention are particularly suitable for use in the hydrocracking of gas oil or fractions thereof. The exact conditions of operation depend partly upon the character of the charge stock and partly upon the activity of the catalyst which is used. Generally the hydrocracking process is conducted at temperatures ranging from 260° to 540° C., a pressure of from about 3.4 to about 100 atmospheres or more, and liquid hourly space velocities (defined as the liquid volume of oil charged per hour per volume of catalyst in the reaction zone) of from about 0.5 to about 20 or more. The hydrocracking reaction is effected in the presence of hydrogen which may be introduced from an extraneous source or recycled from within the process.

The hydrocracking process utilizing the catalyst of the present invention is effected either batch-wise or preferably in a continuous type operation. In a preferred continuous type operation the hydrocarbons to be treated and hydrogen are continuously passed through a fixed bed of the catalyst in either an upward or downward flow. In the moving-bed type of continuous operation the catalyst and hydrocarbons are passed either in concurrent or countercurrent flow through a reaction zone. In a suspensoid type of continuous operation the catalyst and hydrocarbons are passed as a slurry through the reaction zone.

The following Examples are given to further illustrate the catalyst and process of the present invention. The percentages mentioned therein, unless indicated otherwise, are by weight.

EXAMPLE I

In this example 790 g. of water glass (28% SiO_2) was diluted with 1580 cc. of water and added with stirring to 315 cc. of hydrochloric acid plus 630 cc. of water. The acid-silica sol was added to 4075 cc. of $Al_2(SO_4)_3$ solution, said solution having a specific gravity of 1.28 which was prepared from iron-free $Al_2(SO_4)_3xH_2O$ crystals. The alumina-silica sol was then added with vigorous stirring to 1850 cc. of ammonium hydroxide (28% NH_3), the final pH being 8.2. Following this 65 cc. of ammonium hydroxide was added to increase the pH to 8.5. The gel was filtered, cut into small pieces and washed in a glass tube for 24 hours with 7.6 liters of water plus 150 cc. of 1.5 N ammonium hydroxide per hour at 80° C. The gel was dried for a period of about 16 hours at 150° C. and pilled into 3.2 mm. pills. Following this the pills were calcined for an additional 3 hours at a temperature of 650° C. The resulting composite contained about 63 wt. % alumina and 37 wt. % silica.

The metal component of the catalyst was then added by dissolving 2.0 g. of purified palladium chloride in 250 cc. of water plus 12 cc. of hydrochloric acid. The solution was then diluted to 300 cc. with water and poured over 300 g. of the silica-alumina base prepared according to the preceding paragraph in a rotating steam drier. The pills were dried for 2 hours in a steam drier and for 1 hour in a drying oven at 150° C. The dried pills were separated into 4 parts and were oxidized for 1 hour in a muffle oven at various temperatures. The first part which may be designated as catalyst A was oxidized at a temperature of 538° C.; catalyst B at 649° C.; catalyst C at 704° C. and catalyst D at 760° C. Following this all catalysts were reduced in a glass tube with a downflow of 28.3 normal liters hydrogen per hour at 427° C. for one-half hour. The catalyst bed was purged with hydrogen at room temperature. The superiority of the catalysts C and D of the present invention over the catalysts A and B is shown in Example II.

EXAMPLE II

The catalysts which were prepared as set forth in Example I above were used to hydrocrack a White Oil charge stock having a boiling range of from 371° to 482° C. One-hundred cc. of each of the catalysts A, B, C and D were used in four runs under similar conditions, that is a catalyst temperature of 274° C., a pressure of 102 atmospheres, a liquid hourly space velocity of 1 and recycle hydrogen supplied at a rate of 535 cubic meters per cubic meter of charge stock. The reactor was immersed in a fused salt bath which was maintained at approximately the same temperature as that of the reactor. The results of these tests are summarized in Table I.

TABLE I

Catalyst	A	B	C	D
Oxidation temp., °C.	538	649	704	760
Conversion (Volume % distilled at 204° C.)	—	17	20	40

In the following Table the catalysts were used under otherwise identical conditions, but at a series of different temperatures. The comparative conversions (volume percent distilled at 204° C.) at three temperature levels were as follows:

TABLE II

	Conversion (Vol. % distilled) at 204° C.			
Catalyst	A	B	C	D
Operating Temp., °C.				
288	20	29	39	46
302	43	45	55	59
316	62	73	80	80

The same catalysts were also utilized in runs in which the conversion (volume percent distilled) at 343° C. was determined. The results of these runs at four different operating temperatures are shown in Table III.

TABLE III

Catalyst	Conversion (Vol. % distilled at 343° C.) A	B	C	D
Operating Temp., °C.				
274	—	44	57	69
288	52	59	68	76
302	72	74	82	84
316	92	93	95	98

It is therefore evident that the catalyst D, which was calcined at 760° C., exhibited a substantial increase in the conversion or hydrocracking of the charge stock into the desired products at milder operating conditions (lower temperatures of 274° and 288° C.) than did the catalysts which were calcined or oxidized at lower temperatures.

It was also found that the use of catalysts which were oxidized at temperatures of 816°, 871° and 927° C. resulted in relatively good conversion rates. However, the use of these calcination temperatures resulted in shrinkage of the catalyst, with a resultant increase in the apparent bulk density, thereby necessitating the use of a greater weight of catalyst. For example, four 100 cc. catalyst portions produced under otherwise equal conditions but calcined at different temperatures had different relative weights as shown in the following Table:

TABLE IV

Oxidation Temp., °C.	760	816	871	927
Weight of 100—cc. portion	70	73	80	86

EXAMPLE III

A catalyst base was prepared in a manner similar to that set forth in Example I above. Following the recovery of the base in the form of pills, 1.0 cc. of platinum stock solution containing .311 g. of platinum per cc. was diluted to 90 cc. with water plus 2 cc. of hydrochloric acid. The solution was poured over 78 g. of the base pills in a rotating steam drier and dried for 2 hours. Following this the catalyst was divided into 3 portions, catalyst E being oxidized in a muffle oven for 1 hour at 649° C., catalyst F was oxidized at 704° C. and catalyst G at 760° C. Following this the catalysts were then reduced for one-half hour in the presence of hydrogen at a temperature of 427° C. The hydrocracking activities of these catalysts differed in the same way as shown for the analogous catalysts B, C and D in Example II.

EXAMPLE IV

In this example a catalyst base comprising silica-alumina was prepared according to the method set forth in Example I above. Separate hydrocracking catalysts were then prepared by oxidizing nickel nitrate on the silica-alumina at various temperatures. Five separate catalysts were prepared, Catalysts I, II and III were prepared by adding nickel nitrate to the silica-alumina so that 1% nickel was in the finished catalyst and oxidizing at temperatures of 593°, 649° and 704° C., respectively; Catalysts IV and V were prepared by adding nickel nitrate to the silica-alumina so that the finished catalyst contained 6% nickel on the silica-alumina, and by oxidizing at 704° and 760° C., respectively. The oxidation was followed in each case by reducing treatment with hydrogen as set forth in Example I. The hydrocracking activity of these catalysts was tested by treating a White Oil in a manner similar to that set forth in Example II above. That is, a 100 cc. sample of each of the Catalysts I, II, III, IV and V was tested in runs at a temperature of 274° C., a pressure of about 102 atmospheres, a

liquid hourly space velocity of 1 and with recycle hydrogen supplied at a rate of 535 cubic meters per cubic meter of charge stock. A catalyst which comprises .4% palladium on silica-alumina was used as a standard for the hydrocracking activity. The relative activity for hydrocracking of the palladium on silica-alumina was set at 100.

The effect of the oxidation temperatures of the various catalysts on the activity for hydrocracking is shown in the following Table:

TABLE V

Catalyst	Oxidation temperature, °C.	Relative Activity
I	593	100
II	649	109
III	704	133
IV	704	214
V	760	254

It is readily apparent from the above Table that the catalysts which were oxidized at temperatures in the range of from 704° to 760° C. possess a much higher hydrocracking activity than do the catalysts which were oxidized at lower calcination temperatures.

EXAMPLE V

A catalyst base similar to that set forth in Example I above was prepared and ammonium molybdate was added thereto in an amount so that the finished catalyst contained 3% molybdenum on the silica-alumina base. One catalyst was oxidized at 427° C. and the other was oxidized at 704° C. in a muffle oven for a period of one hour. The hydrocracking activity of these catalysts was determined by processing a White Oil having a boiling range of 371° to 482° C. over 100 cc. of each of the catalysts at a temperature of 316° C., a pressure of 102 atmospheres, a liquid hourly space velocity of 1, 2 and 4 and with recycling of 535 cubic meters of hydrogen gas per cubic meter of charge. The catalysts were compared on the basis of the liquid hourly space velocity which gives a 60% conversion boiling at 343° C. These catalysts were compared with a reference catalyst comprising .4% palladium on silica-alumina, having a relative activity of 100. The molybdenum hydrocracking catalyst which was oxidized at 427° C. exhibited a relative activity of 14 as compared to a value of 68 for the molybdenum catalyst which had been oxidized at a temperature of 704° C.

Therefore, it has been shown that catalysts which are calcined at temperatures ranging from about 700° to about 760° C. will possess higher hydrocracking activity than those which are calcined below this temperature range.

Similarly effective hydrocracking catalysts containing a mixture of a Group VI A metal and a Group VIII metal are prepared by impregnating a silica-alumina base which has been prepared according to the method set forth in Example I above with a mixture of nickel nitrate and ammonium molybdate in either an acidic or basic medium, oxidizing the thus prepared pills by heating them in a muffle furnace to a temperature of about 704° C., maintaining them at this temperature in air for a period of about 1 hour, and treating the oxidized pills will hydrogen in the same manner as described in Example I.

WHAT WE CLAIM IS:—

1. A process for preparing a hydrocracking catalyst, characterized in that a refractory solid support having cracking activity and consisting essentially of silica and at least one oxide of the group of alumina, magnesia, zirconia and thoria is impregnated with a solution of at least one of the compounds of the metals of Groups VI A and VIII of the Periodic Table of Elements, said solution constituting the source of an active hydrogenating metal component in the final catalyst, the impregnated support is heated in an oxidizing atmosphere at a temperature substantially in the range of from 700 to 760° C. for a period of from 1 to 8 hours, and the thus oxidized composite is subjected to a reducing treatment with hydrogen at an elevated temperature.

2. Process according to claim 1, characterized in that the refractory support having cracking activity is impregnated with a solution which imparts to the final catalyst the entire active hydrogenating metal component in an amount calculated as metal, of from 0.01 to 20% by weight of the catalyst, the impregnated support is dried and then subjected to the heating in an oxidizing atmosphere, and the oxidized composite is treated with hydrogen at a temperature substantially

liquid hourly space velocity of 1 and with recycle hydrogen supplied at a rate of 535 cubic meters per cubic meter of charge stock. A catalyst which comprises .4% palladium on silica-alumina was used as a standard for the hydrocracking activity. The relative activity for hydrocracking of the palladium on silica-alumina was set at 100.

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It is readily apparent from the above Table that the catalysts which were oxidized at temperatures in the range of from 704° to 760° C. possess a much higher hydrocracking activity than do the catalysts which were oxidized at lower calcination temperatures.

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A catalyst base similar to that set forth in Example I above was prepared and ammonium molybdate was added thereto in an amount so that the finished catalyst contained 3% molybdenum on the silica-alumina base. One catalyst was oxidized at 427° C. and the other was oxidized at 704° C. in a muffle oven for a period of one hour. The hydrocracking activity of these catalysts was determined by processing a White Oil having a boiling range of 371° to 482° C. over 100 cc. of each of the catalysts at a temperature of 316° C., a pressure of 102 atmospheres, a liquid hourly space velocity of 1, 2 and 4 and with recycling of 535 cubic meters of hydrogen gas per cubic meter of charge. The catalysts were compared on the basis of the liquid hourly space velocity which gives a 60% conversion boiling at 343° C. These catalysts were compared with a reference catalyst comprising .4% palladium on silica-alumina, having a relative activity of 100. The molybdenum hydrocracking catalyst which was oxidized at 427° C. exhibited a relative activity of 14 as compared to a value of 68 for the molybdenum catalyst which had been oxidized at a temperature of 704° C.

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Similarly effective hydrocracking catalysts containing a mixture of a Group VI A metal and a Group VIII metal are prepared by impregnating a silica-alumina base which has been prepared according to the method set forth in Example I above with a mixture of nickel nitrate and ammonium molybdate in either an acidic or basic medium, oxidizing the thus prepared pills by heating them in a muffle furnace to a temperature of about 704° C., maintaining them at this temperature in air for a period of about 1 hour, and treating the oxidized pills will hydrogen in the same manner as described in Example I.

WHAT WE CLAIM IS:—

1. A process for preparing a hydrocracking catalyst, characterized in that a refractory solid support having cracking activity and consisting essentially of silica and at least one oxide of the group of alumina, magnesia, zirconia and thoria is impregnated with a solution of at least one of the compounds of the metals of Groups VI A and VIII of the Periodic Table of Elements, said solution constituting the source of an active hydrogenating metal component in the final catalyst, the impregnated support is heated in an oxidizing atmosphere at a temperature substantially in the range of from 700 to 760° C. for a period of from 1 to 8 hours and the thus oxidized composite is subjected to a reducing treatment with hydrogen at an elevated temperature.

2. Process according to claim 1, characterized in that the refractory support having cracking activity is impregnated with a solution which imparts to the final catalyst the entire active hydrogenating metal component in an amount calculated as metal, of from 0.01 to 20% by weight of the catalyst, the impregnated support is dried and then subjected to the heating in an oxidizing atmosphere, and the oxidized composite is treated with hydrogen at a temperature substantially

in the range of from 260 to 540° C. for a period of from one-half to one hour.

3. Process according to claim 2, characterized in that a synthetic support consisting of approximately 63% by weight of alumina and 37% by weight of silica is impregnated with an aqueous solution containing nickel nitrate in an amount which imparts to the final catalyst a nickel content of from 1 to 6% by weight.

4. Process according to claim 2, characterized in that a synthetic support consisting essentially of silica and alumina is impregnated with an aqueous solution containing nickel nitrate and ammonium molybdate.

5. Process according to claim 2, characterized in that a synthetic support consisting essentially of silica and alumina is impregnated with an aqueous solution containing a compound of platinum or palladium.

6. Process according to claim 5, characterized in that a support consisting of approximately 63% by weight of alumina and 37% by weight of silica is impregnated with an aqueous solution containing the compound of platinum or palladium in an amount which imparts to the final catalyst between 0.01 and 10% by weight of platinum or palladium.

7. Process according to any one of the claims 1 to 6, characterized in that the reducing treatment of the oxidized composite is effected in a hydrocracking reaction zone prior to any contact of the composite with the hydrocarbon charge to be converted with the aid of the catalyst.

8. The process of preparing a hydrocracking catalyst as claimed in claim 1 and substantially as described.

9. Hydrocracking catalyst whenever produced by the process of one of the claims 1 to 8.

10. The process of hydrocracking a hydrocarbon oil whenever performed in the presence of a catalyst produced by the process of one of the claims 1 to 8.

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