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**PROCESS OF PREPARING A SILICA-ALUMINA
SUPPORTED GROUP VIII METAL HYDRO-
CRACKING CATALYST**

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This application is a continuation-in-part of my copending application, Serial No. 145,758, filed October 17, 1961, now abandoned, which in turn is a continuation-in-part of my application, Serial No. 14,525, filed March 14, 1960, now abandoned.

This invention relates to a process for the catalytic cracking of petroleum hydrocarbons in the presence of hydrogen. More particularly, it relates to the hydrocracking of relatively high boiling petroleum hydrocarbons in the presence of a novel hydrocracking catalyst to produce petroleum hydrocarbons boiling within the gasoline range.

The various catalytic cracking processes, wherein relatively high-boiling petroleum fractions are subjected to pyrolysis in the presence of acidic catalysts to form more desirable petroleum fractions substantially within the gasoline boiling range, have found wide acceptance in the field of petroleum refining. While the art of catalytic cracking has progressed to a high degree of perfection since its inception, it nevertheless retains certain characteristics which deter from its overall efficiency. For example, carbon deposition on the catalyst, while desirable to a certain extent in the fluidized type of process for heating purposes, amounts on the average to about 7%. It is generally considered that a carbon content of about 3% would serve the requirements of the fluidized process, while of course a fixed bed type of process would be better served by the elimination of substantially all of the carbon deposition.

Furthermore, in addition to the gasoline boiling range products, a cycle stock is recovered which is further separated into a light cycle oil and a heavy cycle oil. The heavy cycle oils are generally recycled for cooling purposes being refractory in nature. The light cycle oil must be disposed of as inferior distillate fuel oil or it must be thermally cracked since recycling to extinction in a catalytic unit leads to prohibitive coke burn-off and large propane and butane yields rather than gasoline. Most catalytic cycle stocks are not satisfactory as high-speed diesel fuels and they are even inferior to the distilled fuel oils currently sold.

It is also well known that charge stocks used in the catalytic cracking process have been selected petroleum stocks. Thus, for example, heavy residual stocks have not been suitable because of their inherent coke-forming characteristics and excessive formation of gaseous products. As a result the availability of suitable cracking stocks has been somewhat restricted. Gasoline yields are further reduced by the formation of C_1 - C_3 gaseous products which accounts in some cases for about 10% of the charge stock.

When the high boiling petroleum hydrocarbon fractions are subjected to cracking conditions in the presence of hydrogen and a suitable catalyst the foregoing limitations on the catalytic cracking process are largely eliminated. While the beneficial features of the hydrocracking process have long been recognized, their application has been hindered by the lack of a suitable catalyst. The catalysts employed must necessarily embody hydrogenation as well as cracking characteristics.

It is an object of the present invention to provide an improved process for the catalytic cracking of heavy petroleum charge stocks in the presence of hydrogen.

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More specifically, the object is to present a process for the catalytic hydrocracking of heavy petroleum fractions in the presence of hydrogenation catalyst deposited on a particular synthetic composite, said composite embodying characteristics which contribute to a high degree of conversion of heavy petroleum hydrocarbon fractions to gasoline boiling range petroleum fractions and/or high quality fuel oils.

By the phrase "gasoline boiling range petroleum fractions" it is intended to refer to those petroleum fractions comprising volatile hydrocarbons which boil substantially continuously in the range of from about 60° F. to about 410° F.

Other objects and advantages of this invention will become apparent in the following detailed specifications.

In one of its broadest aspects this invention embodies a process for the catalytic hydrocracking of a petroleum hydrocarbon which comprises cracking said petroleum hydrocarbon in admixture with hydrogen at hydrocracking conditions in the presence of a catalyst comprising a metal of Group VIII deposited on a synthetic composite of silica and alumina, said silica-alumina composite having been prepared by commingling an alkali metal silicate solution with a sufficient quantity of a mineral acid solution to form an acidic salt-containing silica sol, first gelling and aging the resultant salt-containing sol under acid conditions and then adding an alkaline reagent and further aging the resultant gel under basic conditions, commingling the resultant aged gel with an aluminum salt solution, precipitating a silica-alumina composite therefrom by the addition of a basic precipitant, water-washing the freshly precipitated and undried silica-alumina composite sufficiently to remove from about 10% to about 90% but not all of the water soluble salts therefrom, drying said water-washed silica-alumina composite at a temperature of from about 200° F. to about 500° F., and further water-washing the resultant dried silica-alumina to remove the remaining water soluble salts therefrom prior to a final calcination thereof.

A more specific embodiment is in a process for the catalytic hydrocracking of a petroleum hydrocarbon boiling in the range of from about 400° F. to about 1200° F., which comprises cracking said petroleum hydrocarbon fraction in admixture with hydrogen at a pressure of from about 800 p.s.i. to about 3000 p.s.i. and at a temperature of from about 400° F. to about 800° F. in the presence of a catalyst comprising from about 0.1 to about 10 wt. percent palladium deposited on a synthetic composite of silica and alumina, said silica-alumina composite being prepared by commingling an alkali metal silicate solution with a sufficient quantity of a mineral acid solution to form a salt-containing silica sol having a pH of from about 3.5 to about 4.5, gelling and aging the resultant salt-containing sol at a pH of from about 4 to about 4.5, and then adding an alkaline reagent and further aging the resultant gel at a pH of from about 7 to about 7.5, commingling the resultant aged gel with an aluminum salt solution, precipitating a silica-alumina composite therefrom by adding a sufficient amount of a basic precipitant to raise the pH to about 8, water-washing said silica-alumina composite sufficiently to remove from about 30% to about 60% but not all of the water soluble salts therefrom, forming an aqueous slurry of said water-washed silica-alumina composite and spraying the slurry in an atomized state into an atmosphere of hot inert gases maintained at a temperature of from about 200° F. to about 500° F. to effect a rapid evaporation of the moisture therefrom, and further water-washing the resultant spray dried silica-alumina to remove the remaining water soluble salts therefrom prior to a final calcination thereof at a temperature of from about 800° F. to about 1400° F.

In accordance with the process of this invention a petroleum hydrocarbon fraction boiling in the range of from about 400° F. to about 1200° F. is catalytically cracked in the presence of hydrogen at a pressure of from about 500 p.s.i. to about 3000 p.s.i. and at a temperature of from about 400° F. to about 1000° F.

Petroleum hydrocarbon fractions which can be utilized as charge stocks according to the process of this invention thus include the gas oils, fuel oils, kerosenes, etc., recovered as distillate in the atmosphere distillation of crude oils, also the light and heavy vacuum gas oils resulting from the vacuum distillation of the reduced crude, also the light and heavy cycle oils recovered from the catalytic cracking process, light and heavy coker gas oils resulting from low pressure coking, also coal tar distillates and the like. Residual oils, often referred to as asphaltum oil, liquid asphalt, black oil, residuum, etc., obtained as liquid or semi-liquid residues after the atmospheric or vacuum distillation of crude oils, are operable in this process although it may be desirable to blend such oils with lower boiling petroleum hydrocarbon fractions for economical operation. The petroleum hydrocarbon charge stock may boil substantially continuously between about 400° F. and about 1200° F. or it may consist of any one, or a number of petroleum hydrocarbon fractions, such as are set out above, which distill over within the 400–1200° F. range.

The catalysts of this invention are not deactivated to any appreciable degree by the sulfur impurities which are frequently present in charge stocks such as are utilized in the present process. However, a relatively small amount of nitrogen present in the charge stock has an adverse effect on the process necessitating more severe operating conditions and/or intermittent operation. In order to operate continuously over extended periods of time and under mild operating conditions charge stocks which contain an excess of about 100 p.p.m. nitrogen should be treated to separate the excess nitrogen therefrom. This reduction in nitrogen content can be accomplished by conventional methods such as, for example, acid treatment, treatment with hydrogen under pressure in the presence of catalysts comprising cobalt molybdate, cobalt tungstate, nickel sulfide, etc., or by any other suitable means.

Since the petroleum hydrocarbons which are hydrocracked according to the process of this invention boil over a considerably wide range, it may be readily perceived that suitable reaction temperatures will lie within a correspondingly wide range, the preferred temperature ranges depending in each instance upon the particular petroleum hydrocarbon fraction utilized as a charge stock. For example, reaction temperatures of from about 400° F. to about 1000° F. are generally operable. However, where the particular petroleum hydrocarbon fraction utilized boils within the range of from about 700° F. to about 900° F., it is preferred to operate at reaction temperatures in the more restricted range from about 500° F. to about 700° F.

Hydrogen is reacted with the cracked petroleum hydrocarbon at a pressure of from about 500 p.s.i. to about 3000 p.s.i., or preferably at from about 1200 p.s.i. to about 1800 p.s.i. The ratio of hydrogen to the petroleum hydrocarbon charge stock is from about 5000 s.c.f. to about 15,000 s.c.f. per barrel of charge stock although amounts of from about 1000 s.c.f. to as much as 30,000 s.c.f. per barrel are operable. The liquid hourly space velocity of the petroleum hydrocarbon charge stock can be from about 0.1 to about 10 depending on the particular charge of employed and the reaction temperatures necessitated thereby. A suitable correlation between space velocity and reaction temperature can be readily determined by one skilled in the art in any particular instance. When utilizing the charge stock boiling in the range of from about 700° F. to about 900° F., a liquid hourly space velocity of from about 1.0 to about 3.0 is preferred.

A synthetic silica-alumina composite upon which a metal of Group VIII is deposited is particularly adapted to the process of this invention. Several alternative procedures are available for the preparation of the silica-alumina composite. In one method, a suitable mineral acid, such as sulfuric acid, hydrochloric acid, or nitric acid, is added to an aqueous solution of an alkali metal silicate, sodium silicate being preferred because of its low cost and ready availability. In a second method the order of addition is reversed, the water glass being added to the acid; this technique is preferred since formation of the silica sol always occurs under acid conditions and there is little danger of the sol solidifying prematurely as is the case in the former method when the pH of the system is being reduced from a high value to a low value. When using sulfuric acid, concentrations thereof from about 10% to about 30% are satisfactory. The water glass solution may be prepared from commercial sodium silicates such as Philadelphia Quartz Company, brands E, M, N, or S; the commercial water glass is first diluted with water to reduce the silica concentration thereof to from about 5% to about 15% by weight. The volumetric quantities and concentrations of the reactants should be adjusted to yield, upon mixing of acid and water glass, a silica sol containing from 20 to 80 grams of silica per liter of sol, and at a pH of from about 3.5 to about 4.5. The commingling of acid and water glass is preferably carried out relatively slowly, and with stirring, a mixing time of about 45 minutes being adequate therefor.

After the acid and water glass have been commingled, the resultant silica sol is allowed to age at a pH of from about 4 to about 4.8, and preferably 4 to 4.5 or more advantageously 4 to 4.2 for at least 2.5 hours. The sol will become a viscous hydrogel within a period of 5 minutes to 2 hours, depending upon its composition, initial pH, extent of dilution, aging temperature and other factors. Due care should be exercised during this period to prevent the gel from solidifying, which can be accomplished by stirring or agitating the gel and by adding quantities of water if necessary. Following the acid aging treatment sufficient alkaline reagent, e.g. NH_4OH , is added to raise the pH of the gel to basic or near basic conditions, that is, to a pH of at least 6.5 and preferably to a pH of from 7.0 to 7.5, or still more advantageously from about 7.0 to about 7.2, and the gel is further aged under such basic conditions for at least one hour.

Upon completion of the basic aging period, sufficient aluminum salt, e.g. aluminum sulfate, aluminum chloride, aluminum nitrate, etc. is added to the silica gel, with mixing, to provide a final catalyst composite, containing from about 1% to about 50%, and preferably from about 10% to about 30%, alumina. This may be conveniently accomplished by the addition of a 20%–30% aluminum sulfate solution. After thoroughly impregnating the aluminum salt into the silica gel, a basic precipitating agent is then added to increase the sol pH to 8.0–8.5, at which point the aluminum hydrolyzes and homogeneous precipitation of a silica-alumina composite occurs. A suitable basic precipitant is a 10%–15% ammonium hydroxide solution, although other basic mediums such as potassium hydroxide, sodium hydroxide, ammonium carbonate, alkyl amines, etc. may be employed when desired. At this stage, the silica-alumina composite exists as a gel slurried in a mother liquor. The slurry contains a considerable quantity of soluble salts, e.g. sodium sulfate, and/or ammonium sulfate, as reaction products of the water glass, acid, and base. It is essential that the silica-alumina composite be recovered substantially free of the salts prior to utilization as a catalyst and/or catalyst support. This is generally accomplished by filtering the mother liquor from the gel and subjecting the gel to repeated water-washings. Prior art methods generally teach that water-washing may be

accomplished in whole or in part before drying of the gel or in whole or in part subsequent thereto, and attach no particular significance to the order of washing and drying with respect to the intended use of the finished catalyst. However, it has now been discovered that a correlation does exist between the order of washing and drying of the composite and the intended use of the finished catalyst when the intended use is in hydrocracking of petroleum hydrocarbons. It has been found that separation of the salts in a manner whereby only a portion of the salts, say from about 10% to about 90%, are removed prior to drying at a temperature of from about 200° F. to about 500° F. and removing substantially all of the remainder subsequent to drying, will yield a silica-alumina composite which, when composited with the catalytically active materials hereinafter defined, will form a substantially improved hydrocracking catalyst. For example, as will become apparent from the appended examples, when the silica-alumina slurry is dried prior to removal of any of the salts therefrom an inferior hydrocracking catalyst results therefrom. Similar results are obtained where substantially all of the salts are removed prior to drying. However, where only a portion of the salts, say from about 10% to about 90%, are removed prior to drying at a temperature of from about 200° F. to about 500° F., a considerably improved hydrocracking catalyst is obtained.

Removal of a suitable portion of the salts can be accomplished simply by the separation of the above mentioned mother liquor from the silica-alumina dispersed therein by decantation, filtration or any other conventional means. The silica-alumina can be re-slurried in water and filtered a number of times to reduce the salt content thereof to any desired level. It is preferred to remove from about 30% to about 60% of the soluble salts prior to drying of the silica-alumina composite.

The silica-alumina composite is preferably dried by spray drying methods wherein an aqueous slurry of silica-alumina gel is sprayed in an atomized state into an atmosphere of hot inert gases to effect a rapid evaporation of the moisture therefrom. The drying step is carried out at a temperature of from about 200° F. to about 500° F. The dried silica-alumina is then subjected to multiple stage washing to separate the balance of the soluble salts therefrom. It is desirable to include in the multiple stage washing, a washing step utilizing a dilute (0.01%–0.1%) ammonium salt solution, such as an aqueous ammonium chloride solution, to effect the removal of alkali ion, such as sodium ion, followed by a water wash. The silica-alumina composite is then dried, and calcined at a temperature of from about 800° F. to about 1400° F.

The above described silica-alumina composite is impregnated with a metal of Group VIII of the Periodic Table which includes platinum, palladium, iridium, osmium, rhodium, ruthenium, nickel, iron and cobalt. In one preferred embodiment of this invention palladium is utilized. In another preferred embodiment nickel is employed.

Impregnation with the Group VIII metal can be accomplished by any suitable or conventional methods. For example, the silica-alumina is immersed in an aqueous solution of chloroplatinic acid, bromoplatinic acid, platinum chloride, palladium chloride, chloropalladic acid, etc., or an aqueous solution of a salt of iron, nickel, cobalt, such as ferric chloride, ferric bromide, ferric fluoride, ferric nitrate, ferric sulfate, ferric formate, ferric acetate, etc., cobalt nitrate, cobalt fluoride, cobalt iodide, cobalt bromide, cobalt chloride, cobalt acetate, cobalt formate, etc., nickel chloride, nickel bromide, nickel iodide, nickel fluoride, nickel nitrate, nickel sulfate, nickel acetate, nickel formate, etc., such that the liquid is substantially taken up by the silica-alumina, the concentration of the solution being such as to insure a metal deposit of from about 0.1% to about 10% by weight of the final catalyst. The catalyst is then dried, usually at temperatures at from

about 200 to about 350° F., and calcined. When so desired, the catalyst preparation may be completed by reduction with hydrogen or other methods known to the art, or it may be so reduced immediately prior to use.

The process of this invention can be carried out by conventional methods and utilized standard equipment. For example, a system comprising a moving catalyst bed wherein the reactant flow may be concurrent or counter-current to the catalyst flow can be utilized, or the catalyst may be contained in a fixed bed reactor. In the fixed catalyst bed system the petroleum hydrocarbon and hydrogen reactants are charged to a suitable high pressure reactor equipped with heating means and containing therein a fixed catalyst bed comprising the catalyst of this invention. Said reactants can be commingled before entering the reactor or they can be charged thereto in individual and separate streams; also the reactants may be charged in an upflow or in a downflow manner. The reactor effluent is collected in a high pressure separator wherein the hydrocarbon products are separated and the excess hydrogen recovered for recycle purposes and recycled by means of a recycle compressor.

The following examples are presented for the purpose of illustrating the process of the present invention and it is not intended to thereby limit the generally broad scope of this invention.

EXAMPLE I

A silica-alumina gel was prepared by first diluting 135 ml. of concentrated sulfuric acid with 400 ml. of water. 1610 grams of water glass was diluted with 3220 ml. of water and added with stirring to the diluted sulfuric acid over a 30 minute period. The final pH was 3.3. After one hour of stirring, the sol became viscous and 3230 ml. of water was added thereto. 6000 ml. of water and 15 ml. of ammonium hydroxide was then added to bring the pH of the sol to 7.0. The sol was stirred at this pH value for one hour after which 1570 ml. of an aluminum sulfate solution (sp. gr. 1.28) was added. The pH at this point was 3.2. 640 ml. of ammonium hydroxide and 640 ml. of water was added to the sol bringing the pH to 8.0. The gel was slurried for about 15 minutes. At this point the slurry was separated into three portions hereafter designated as A, B and C.

The portion of the above described slurry designated as "A" was spray dried without further treatment. The spray dried material was thereafter slurried about five times in 2 liters of water and 20 ml. of 5% ammonium chloride, and one more time in 2 liters of water to remove substantially all of the soluble salts therefrom. The resultant silica-alumina composite was then dried at 300° F., made into 1/8" pills and calcined for three hours at 1200° F. The resultant composite contained about 1.5 wt. percent sulfate.

A second portion of the above described slurry designated as "B" was filtered, thereby removing about 1/3 of the soluble salts, and the residue was reslurried in water. This slurry of the filtered silica-alumina gel was spray dried, and further treated as was "A" previously. The resultant composite contained about 1.3 wt. percent sulfate.

The third portion of the above described slurry designated as "C" was filtered and the residue reslurried in water and further filtered. This procedure was repeated until the filtrate was substantially free of soluble salts. The salt-free silica-alumina gel was then reslurried in water, spray dried, and further treated as was "A" previously. The resultant composite contained about 0.6 wt. percent sulfate.

The 1/8" silica-alumina pills prepared as above described comprise about 75% silica and about 25% alumina. All three batches, designated "A," "B" and "C" were further impregnated with palladium such that the palladium was present to the extent of 0.4% of the final catalyst weight.

The above described catalysts were evaluated as to hydrocracking activity by means of a relative activity test. The test comprises processing a 340 white oil (28.6° API, boiling range 690°–875° F.) and 3000 s.c.f./bbl. recycle hydrogen over 100 cc. of a "standard" hydrocracking catalyst in a fixed bed, said catalyst comprising 0.4% palladium in commercial 25% Al₂O₃ cracking catalyst. The white oil was processed over the catalyst at a LHSV of 1, 2 and 4. In each case the liquid product was subjected to Engler distillation to determine the percent over at 650° F. and the result was plotted against liquid hourly space velocity (LHSV). The "standard" catalyst was arbitrarily assigned an activity of 100. The results are tabulated below and illustrate the hydrocracking capacity of the "standard" catalyst.

Table I

Liquid Product:	1	2	4
LHSV	54.9	47.9	39.7
API gravity			
Engler dist.:			
Percent at 180° F.	16.5	8.2	1.3
Percent at 400° F.	62.7	42.1	20.1
Percent at 650° F.	85.1	69.9	43.0
Carbon on Catalyst, wt. percent			1.15
Gaseous Product, wt. percent:			
C ₁ –C ₃	0.9	0.5	0.3
C ₄	1.9	1.3	0.9

¹ Carbon on catalyst is the result of a thirty hour test comprising test runs at 1, 2, and 4 LHSV.

The hydrocracking activity of the sample catalyst was then determined by processing the white oil over the sample catalyst at the aforesaid conditions, subjecting the resulting liquid products to Engler distillation to determine the percent over at 650° F., and plotting the result against LHSV. The relative activity of the sample catalyst was then determined as the ratio of the LHSV required to yield a liquid product 60% of which distills over at 650° F., to the LHSV required for the same yield in the presence of the standard catalyst. The relative activity number is the fraction representing the aforesaid ratio, multiplied by the activity of the standard catalyst (100). The results of the relative activity tests of the catalysts A, B and C of Example I are tabulated below:

Table II

Catalyst	A			B			C		
Relative activity	27			147			49		
Liquid Product:									
LHSV	1	2	4	1	2	4	1	2	4
API gravity	41.7	36.0	32.9	61.1	52.3	42.8	45.6	39.9	34.2
Engler dist.:									
Percent at 180° F.	0.5	0	0	17.5	9.0	7.0	2.5	0	0
Percent at 400° F.	29.5	14.0	8.0	84.0	67.0	37.0	38.5	22.5	11.5
Percent at 650° F.	58.5	33.0	20.0	96.0	87.0	60.0	70.0	49.0	27.0
Carbon on Catalyst, wt. percent			1.51			1.85			1.94
Gaseous Product, wt. percent:									
C ₁ –C ₃	0.2			1.0			0.4		
C ₄	0.5			3.2			0.6		

¹ Carbon on catalyst is the result of a thirty hour test comprising test runs at 1, 2, and 4 LHSV.

It is apparent that hydrocracking of petroleum hydrocarbons according to the process of this invention results in an excellent yield of products falling within the gasoline range with a minimum formation of coke and C₁–C₃ hydrocarbons. The data further points out that water-washing the freshly precipitated silica-alumina gel sufficiently to remove only a portion of the soluble salts prior to drying of the silica-alumina composite as herein taught, results in a more active hydrocracking catalyst than is the case where the salts are substantially completely removed either before or after drying. Comparison of the results obtained from the testing of catalyst B and C show that catalyst B, prepared according to the method of this invention, is by far the more active hydrocracking catalyst

even though the final sulfate content thereof is in considerable excess of catalyst C.

The data set out in the foregoing table is the result of a once-through operation. The product recovered from this once-through operation contains a hydrocarbon fraction boiling in excess of the gasoline boiling range. This hydrocarbon fraction can be economically utilized as a high grade fuel oil or it can be recycled for increased gasoline yields as it is excellent charge stock for the hydrocracking process.

I claim as my invention:

1. A process for the preparation of a silica-alumina supported Group VIII metal hydrocracking catalyst which comprises commingling an alkali metal silicate solution with a sufficient quantity of a mineral acid solution to form an acidic-salt-containing silica sol, first gelling and aging the resultant salt-containing sol under acid conditions, and then adding an alkaline reagent and further aging the resultant gel under basic conditions, commingling the resultant aged gel with an aluminum salt solution, precipitating a silica-alumina composite therefrom by the addition of a basic precipitant sufficient to raise the pH to at least 8, water washing the freshly precipitated, undried silica-alumina composite sufficiently to remove from about 10% to about 90% but not all of the water soluble salts therefrom, drying said water washed silica-alumina composite at a temperature of from about 200° F. to about 500° F., further water washing the resultant dried silica-alumina composite sufficiently to remove the remaining water soluble salts therefrom, calcining the thus purified silica-alumina composite at a temperature of from about 800° F. to about 1400° F., and impregnating the calcined silica-alumina composite with a Group VIII metal catalytic component.

2. The process of claim 1 further characterized in that the pH of said silica sol during the acid aging thereof is maintained in the range of from about 4 to about 4.5.

3. The process of claim 2 further characterized in that said alkali metal silicate solution is added to said mineral acid solution until the pH of the resultant silica sol is in the range of from about 3.5 to about 4.5.

4. The process of claim 3 further characterized in that the pH of said silica gel during the basic aging thereof is maintained in the range of from about 7.0 to about 7.5.

5. A process for the preparation of a silica-alumina supported Group VIII metal hydrocracking catalyst which comprises commingling an alkali metal silicate solution with a sufficient quantity of a mineral acid solution to form a salt-containing silica sol having a pH of from about 3.5 to about 4.5, gelling and aging the resultant salt-containing sol at a pH of from about 4 to about 4.5, and then adding an alkaline reagent and further aging the resultant gel at a pH of from about 7 to about 7.5, commingling the resultant aged gel with an aluminum salt solution, precipitating a silica-alumina composite therefrom by adding a sufficient amount of a basic precipitant to raise the pH to about 8, water washing said silica-alumina composite, prior to drying thereof, sufficiently to remove from about

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10% to about 90% but not all of the water soluble salts therefrom, forming an aqueous slurry of said water washed silica-alumina composite and spraying the slurry in an atomized state into an atmosphere of hot inert gases maintained at a temperature of from about 200° F. to about 500° F. to effect a rapid evaporation of the moisture therefrom, further water washing the resultant spray dried silica-alumina composite sufficiently to remove the remaining water soluble salts therefrom, calcining the thus purified silica-alumina composite at a temperature of from about 800° F. to about 1400° F., and impregnating the calcined silica-alumina composite with a Group VIII metal catalytic component.

6. The process of claim 1 further characterized in that from about 30% to about 60% of the water soluble salts are removed from said freshly precipitated, undried silica-

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alumina composite by the first-mentioned water washing step.

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