United States Patent Office

3,067,127
Patented Dec. 4, 1962

3,067,127

CATALYTIC HYDROCRACKING WITH THE USE OF A SILICA-ZIRCONIA COMPOSITE

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No Drawing. Filed Jan. 6, 1960, Ser. No. 703
20 Claims. (Cl. 208—110)

This invention relates to the catalytic conversion of hydrocarbons and to an improved catalyst for effecting said conversion. More specifically, the invention is concerned with catalytic hydrocracking of hydrocarbon oils in the presence of a new and improved catalyst. In one embodiment, the invention is concerned with an improved hydrocracking catalyst consisting essentially of at least one component characterized by dehydrogenation activity deposited on a particularly prepared silica-zirconia base. In another embodiment, the invention is directed to an improved method for preparing the aforesaid catalyst useful in catalytic cracking of heavy petroleum fractions in the presence of hydrogen to lighter materials boiling in the gasoline range.

As is well known, cracking refers generally to operations wherein a long chain hydrocarbon or a mixture of high molecular weight hydrocarbons is converted into a shorter chain hydrocarbon or into a mixture of lower molecular weight hydrocarbons. Cracking, accomplished solely as a result of the high operational temperature employed, is known as thermal cracking while cracking effected in the presence of catalysts is ordinarily known as catalytic cracking. Cracking carried out in the presence of hydrogen is referred to as hydrocracking.

Catalytic cracking of petroleum hydrocarbons has heretofore been carried out at temperatures in the range of 800 to 1100° F. Such high temperatures have been inefficient from an economical standpoint and undesirable from an operational standpoint resulting in the production of unwanted coke, relatively large amounts of dry gas and excess quantities of C_4 hydrocarbons. The production of coke and dry gas represents a loss thereby bringing about an overall decrease in the yield of useful cracked product.

As is well known, charge stocks heretofore employed in catalytic cracking operations have been selected petroleum stocks. Thus, heavy residual stocks as well as cycle stocks obtained from catalytic cracking of known refractory petroleum cracking stocks have not been suitable for catalytic cracking processes because of their inherent coke-forming characteristics and the excessive amounts of dry gas produced. Accordingly, the supply of available cracking stocks has been somewhat restricted.

Cracking operations carried out in the presence of hydrogen at relatively high temperatures and under elevated pressures, i.e. hydrocracking, do not impose the aforesaid limitations on the type of useable charge stock. Thus, cycle stocks, heavy residuals etc. can be cracked in hydrocracking operations. Conventional operations of this type, however, have many disadvantages. Thus, in order to maintain catalyst activity at a desired level and to avoid a heavy deposition of coke on the catalyst, it has been necessary to employ excessively high hydrogen pressures of the order of at least about 3000 pounds per square inch and preferably much higher.

There is accordingly, at the present time, great interest in the petroleum industry in developing a moderate pressure hydrocracking process. This interest arises from the ability of hydrocracking to substantially increase both the quantity and quality of naphtha and fuel oil that a petroleum refinery can produce from crude oil. These advantages have been amply demonstrated by the aforementioned high pressure hydrocracking operations. The high cost of high pressure hydrocracking necessitating the use of expensive high pressure equipment has prevented its widespread use, hence the necessity in developing a less expensive moderate pressure process which will retain many of the demonstrated advantages but at acceptable cost.

In accordance with the present invention, it has been discovered that cracking of hydrocarbons in the presence of hydrogen and a particular catalyst permits the use of appreciably lower reaction temperatures and pressures. Thus, it has been found that cracking of hydrocarbons can be effected in the presence of hydrogen and in the presence of a catalyst comprising a particularly prepared support consisting essentially of silica and zirconia and having impregnated thereon a minor proportion of a dehydrogenation component. Such catalyst employed in the process of the invention has been found to afford a highly favorable distribution of products of high quality. The process described herein has the further advantage of being applicable for catalytic hydrocracking a wide variety of charge stocks including heavy residual and refractory charge stocks.

The present invention provides a process for hydrocracking a hydrocrackable material by contacting the material to be hydrocracked and, particularly, a petroleum hydrocarbon fraction having an initial boiling point of at least about 400° F., a 50 percent point of at least about 500° F. and an end boiling point of at least about 600° F. and boiling substantially continuously between said initial boiling point and said end boiling point with the above catalyst consisting essentially of particularly prepared silica-zirconia having deposited thereon a minor proportion of a component characterized by dehydrogenation activity in the presence of hydrogen at a hydrogen partial pressure between about 100 and about 5,000 pounds per square inch gauge, a liquid hourly space velocity of between about 0.1 and about 10, a temperature between about 600° F. and about 1050° F. employing a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80.

We are aware that it has heretofore been proposed to convert hydrocarbon fractions in the presence of hydrogen and certain catalytic composites consisting essentially of a cracking component of silica combined with alumina, zirconia, magnesia and the like, which has undergone impregnation with a minor proportion of a dehydrogenation component such as platinum, molybdena, etc. The hydrocracking process described herein is distinguishable from such prior processes in that the silica-zirconia base upon which the dehydrogenation component is deposited is prepared in accordance with a particular procedure which has been found to result, after the aforesaid impregnation, in a more active, stable and selective hydrocracking process.

Thus, catalysts heretofore proposed for hydrocracking operations have consisted almost entirely of active hy-

drogenating components dispersed on an existing active cracking base such as platinum on silica-alumina, molybdena on silica-alumina, or of supported metal oxides or sulfides that have, to varying degrees, both hydrogenating and cracking activity such as nickel sulfide on alumina, tungsten disulfide on clay and the like. Neither of the above type catalysts has proven satisfactory for moderate pressure hydrocracking. When tested, these catalysts have shown a lack in one or more of the following: the ability to retain activity during use; a good balance between cracking and hydrogenating activities; or the recovery of activity when carbonaceous products are removed after a period of use.

Following the teachings of this invention, it has been found that highly effective catalysts for use in moderate pressure hydrocracking can be obtained by impregnation of a dehydrogenation component on a composite of silica and zirconia which has been prepared by reacting a water-soluble zirconium compound and an alkali metal silicate to effect formation of a gelable sol consisting essentially of silica and zirconia characterized by a pH in excess of 6 and a zirconia content, on a dry solids basis, of between about 2 and about 20 percent by weight, permitting the sol to set forming a silica-zirconia gel, reducing the pH of the gell to below 5 and activating the same by maintaining the gell under such conditions of reduced pH while in contact with an aqueous medium at a temperature in the approximate range of 150 to 220° F. for a period of at least about 1 hour under conditions of substantially atmospheric pressure, thereafter washing the gel free of soluble matter, drying and calcining. A catalyst prepared in accordance with the foregoing procedure has been found to be capable of affording unexpected performance in hydrocracking petroleum fractions at moderate pressures, i.e. generally not in excess of a hydrogen partial pressure of about 5000 pounds per square inch gauge.

In the foregoing procedure it has been discovered that the activation step of treating the silica-zirconia gel in an aqueous medium at the specified conditions and the control of pH during gelation and such activation step are essential in achieving the usually effective activity, stability and selectivity characterizing the catalyst described herein. It has been found, in accordance with the present invention, that not only is the activation step essential but that also the conditions required during this step to obtain the above-described desirable catalyst properties are very critical. Thus, the pH during the activation step is essentially below 5 and preferably below 3. The pH of gel formation, on the other hand, is essentially above 6 permitting the attainment of silica-zirconia gels characterized by particularly favorable gel properties as well as by a short time of set, i.e. generally less than 2 hours and more particularly, less than 20 seconds. Hydrogels prepared at a pH above 6 are much more susceptible to activation than those prepared below 6 pH. The temperature of the activation treatment involving the use of an aqueous medium is above about 150° F. and preferably above 175° F. and generally does not exceed 220° F. The time required for activation is generally at least 1 hour and may extend up to 48 hours or longer. Preferably, the activation period is at least 2 hours and usually in the approximate range of 2 to 24 hours.

The intermediate hydrogel state obtained in preparation of present catalysts is to be distinguished from a gelatinous precipitate. True all-embracing hydrogels occupy the entire volume of the solution from which they are formed and possess a definite rigid structure. When fractured, a true hydrogel shows a conchoidal fracture as compared to an irregular ragged edge fraction as obtained in the case of gelatinous precipitates. The latter occupy only a part of the volume of the solution from which they are formed and have no rigidity of structure. In addition, hydrogels can generally be more easily washed

free of soluble impurities due to the tendency of gelatinous precipitates to peptize on washing. A distinct and further advantage of hydrogels is that due to their rigid structure, they can be formed into high quality spheroidal particles.

The zirconium compound employed in the present process is a water-soluble compound and suitably a water-soluble mineral acid salt of zirconium such as, for example zirconium nitrate; zirconium sulfate and zirconyl chloride. Of this group, zirconium sulfate is accorded preference. Zircon sand is a suitable source of zirconium compound. The zirconia content of such sand can be converted to zirconium sulfate through caustic fusion at temperatures exceeding 1000° F. and subsequent leaching with sulfuric acid.

The silicate reactant is generally an alkali metal silicate and particularly sodium silicate although silicates of the other alkali metals such as for example, potassium silicate, might likewise be employed. An organic silicate ester, for example ethyl orthosilicate may also be employed as the source of silica.

The solutions of zirconium compound and silicate reactant are intimately mixed in such proportions as to yield a gelable sol having a zirconia content, on a dry basis, of between about 2 and about 20 and preferably between about 5 and about 15 percent by weight and a pH of above 6 and generally not exceeding about 10.

The resulting product is a hydrosol of silica and zirconia characterized by an inherent capacity to set to a hydrogel upon lapse of a suitable period of time extending from a few seconds up to several hours depending on pH, temperature and solids concentration without addition to or subtraction from the hydrosol of any substance. By following the above procedure the time of gelation can be very rapid, i.e. less than 20 seconds, which permits the gel to be prepared directly in the form of spheroidal particles resulting in a product of improved physical properties and in definite economic advantages in the manufacture of the catalyst. In addition to affording rapid gelation, the high pH of gel formation has been found to give rise to a more selective hydrocracking catalyst upon impregnation with a dehydrogenation component as described hereinbelow as compared with a comparable silica-zirconia gel in which the pH of formation is below 6.

The silica-zirconia hydrogel so obtained is thereafter treated to reduce the pH thereof to below 5 and preferably less than 3 but greater than 1. To accomplish such purpose, the hydrogel is contacted with an acidic fluid after formation. While the lapse of a brief interval of time is permissible, it is generally desirable to reduce the pH of the silica-zirconia hydrogel shortly after formation to less than 5. Maintaining the hydrogel upon conditions of pH at which formation is effected for a considerable period of time was found to be detrimental to the selectivity of the finished catalyst. Generally, the hydrogel is contacted with an aqueous solution of an acid or an acidic salt of sufficient concentration to effectively reduce the hydrogel pH to less than 5. Usually, an inorganic acid and particularly a dilute solution of a mineral acid such as nitric, hydrochloric or sulfuric acid in the form of a 0.1 to 10 weight percent solution is employed for this purpose. Salts such as sulfates, nitrates or chlorides of zirconium or aluminum can similarly be used.

The hydrogel of reduced pH is then activated by maintaining the same under the aforementioned conditions of reduced pH while in contact with an aqueous medium at a temperature in the approximate range of 150 to 220° F. and more particularly, between about 175 and about 220° F. at substantially atmospheric pressure for at least 1 hour and generally not exceeding about 48 hours. This step is critical in achieving the desired silica-zirconia composite upon which a dehydrogenation component is subsequently deposited. In accordance with such step,

the hydrogel is suitably covered with an acidic solution to maintain the pH of the hydrogel during activation within the approximate range of 1 to 5 and preferably 1 to 3. While the hydrogel after treatment to reduce its pH of formation as described may be transferred or conducted to an aqueous medium maintained at the elevated temperature specified hereinabove, it is generally preferred to effect activation of the hydrogel in the same solution used for reduction of pH. Thus, it is contemplated that in a preferred operation the silica zirconia hydrogel after formation at a pH in excess of 6 is conducted to an aqueous dilute solution of an acid or acid salt wherein the pH of the hydrogel is immediately brought to below 5 and the hydrogel is thereafter maintained in such solution at a temperature of between 150 and 220° F. for a sufficient period to accomplish the desired activation. The pH of the hydrogel during the activation treatment is an important factor having a direct bearing on the ultimate catalyst activity and, in accordance with the process of catalyst preparation described herein, should be less than 5 and preferably below 3 in order to obtain a catalyst of high cracking activity.

After the activation treatment, exchangeable or zeolitic impurities, if present, are removed from the hydrogel in any feasible manner. While as a practical matter all or a large proportion of such zeolitic impurities may be removed during the course of the activation treatment with the aqueous medium containing an acidic compound, any remaining zeolitic matter is suitably removed by base-exchange with aqueous solutions of mineral acids such as hydrochloric and sulfuric acids; solutions of ammonium salts which act to replace metal impurities with ammonium which is later removed by calcining; and solutions of multivalent metal salts particularly a zirconium salt which may be the same or a different zirconium salt from that employed in initial formation of the hydrogel. When base exchanging the silica-zirconia hydrogel with an acid a limited and controlled amount must obviously be used to avoid redissolving the zirconia. When exchanging with ammonium compounds any excesses will be calcined out in the final steps of catalyst manufacture and when using any zirconium or other multivalent metal salt which does not adversely affect the catalytic properties, excesses may be used and left on the composite.

After removal of zeolitic impurities the hydrogel is washed free of soluble excess ions. The resulting composite of silica and zirconia is dried in air or superheated steam at temperatures between about 200 and about 400° F. for a period of between about 4 and 24 hours and/or by calcining at a temperature between about 800 and about 1800° F. for approximately 2 to 8 hours or more.

In some instances, it may be desirable to introduce into the silica-zirconia hydrosol a quantity of solid powdered material insoluble therein having a weight mean particle diameter of between 1 and 5 microns and preferably between 2 and 4 microns. The amount of powdered material so introduced is generally between about 2 percent and about 40 percent by weight and preferably between about 15 and about 40 percent by weight of the dried gel product. The powder-containing silica-zirconia sol sets to a hydrogel after lapse of a suitable period of time and the resulting hydrogel is processed as described above and then dried to a gel at a temperature below the fusion point of the incorporated powder. It has been found that a silica-zirconia gel resulting from the setting of a sol containing powdered material of the aforementioned particle size and drying of the resulting hydrogel at a temperature below the fusion point of the added material has a substantially greater resistance to attrition and improved diffusivity as compared with the corresponding silica-zirconia gels which do not contain such added powder. The powdered material may be added by dispersing in an already prepared hydrosol or as is preferable, when the hydrosol is characterized by a short time of gelation, the powder may be added to one or more of the reactants used in forming the hydrosol or may be mixed in the form of a separate stream with streams of the hydrosol-forming reactants in a mixing nozzle or other means where the reactants are brought into intimate contact. In addition to having the above particle size, the powdered solid incorporated into the silica-zirconia hydrosol should necessarily be insoluble therein and should further be characterized by being infusible at the hydrogel drying temperature. The powder incorporated in the silica-zirconia sol may be catalytically active or an inert material. As indicated hereinabove, the particular powdered material to be incorporated in the hydrosol will be chosen so as to be insoluble therein and to be infusible at the drying temperature. Observing these features, suitable representative materials having a weight mean particle diameter of 1 to 5 microns include gels or gelatinous precipitates such as those of silica, alumina, magnesia, chromia, molybdena, zirconia, thoria, titania and the like including composites thereof. Thus, a particularly prepared powdered material for incorporation in the sol includes pulverized silica-zirconia fines having a weight mean particle diameter of 1 to 5 microns. Other suitable materials include zircon sand (zirconium silicate) as well as other metal silicates, metals and metal oxides including aluminum oxide, chromium trioxide, molybdenum oxide, magnesium oxide, manganese oxide, zirconium oxide and silicon oxide in their various forms and modifications.

The silica-zirconia gel base may be prepared in any desired mechanical form according to the specific purpose for which it is intended. Either before or after calcination, it can be broken into lumps or granules or it can be ground to a fine powder adapted for use in the suspensoid or fluidized-solids process. Alternatively, the catalyst can be formed into pills, pellets or other suitable shapes preferably prior to the calcination step for use in the fixed bed or compact moving bed operations. In this case, the catalytic mixture is partially dried, ground to a powder preferably smaller than 30 mesh (Tyler), combined with a suitable lubricant such as graphite, hydrogenated coconut oil, stearic acid, rosin or the like and shaped by extrusion, molding or by other means known in the art. Particles having dimensions ranging from about ⅛" x ⅛" to ½" x ½" are generally satisfactory. The shaped particles can then be further dried and/or calcined as described above.

It is particularly desirable to prepare the silica-zirconia gel base in the form of spheroidal bead-like particles. For such purpose, the initially prepared hydrosol is introduced in the form of globules to a water-immiscible fluid such as into a column of water-immiscible liquid, for example an oil medium wherein the globules of hydrosol set to spheroidal bead-like particles of hydrogel. Larger size spheres are ordinarily within the range of from about 1/64" to about ½" in diameter, whereas smaller size spheres which are generally referred to as microspheres are within the range of from about 10 to about 100 microns in diameter. The use of spheroidal shaped gel particles is of particular advantage in hydrocarbon conversion processes including the moving catalyst bed process, the fluidized process and other processes in which the spheroidal catalyst particles are subjected to continuous movement. As applied to the stationary bed, spheroidal catalyst particles provide effective contact between the reactants and the catalyst by avoiding channeling.

The conventional cracking activity of a catalyst is generally expressed in terms of the percent by volume of a standard hydrocarbon charge which is cracked under specific conditions in the Cat-A test. The method of this test is described in National Petroleum News, 36 p. PR–537 (August 2, 1944), and the cracking activity so

determined is referred to as the activity index (A.I.). Accordingly, it will be understood that the term "activity index" when employed herein shall refer to the cracking activity of the material under consideration determined in accordance with the Cat-A method. The activity index of the above-described silica-zirconia composites utilized herein as supports for a dehydrogenation component is preferably within the range of about 25 to about 50.

A component exhibiting dehydrogenation activity is deposited on the silica-zirconia gel prepared in accordance with the above-defined procedure. Suitable dehydrogenation components include one or more of the metals of groups V, VI and VIII of the periodic table either in elemental form or in the form of the oxides or sulfides of these metals. Representative of these metals are molybdenum, chromium, tungsten, vanadium, cobalt, nickel and metals of the platinum group, i.e. platinum, palladium, rhodium, osmium, iridium, and ruthenium as well as combinations of these metals, their oxides or sulfides. Thus, a particularly desirable combination of metal oxides is that of the oxides of cobalt and molybdenum deposited on the hereinabove described silica-zirconia base. Deposition of one or more of the above-indicated metals may be in accordance with methods known to the art. For example, aqueous solutions of water-soluble compounds of the desired metal may be employed to impregnate the silica-zirconia composite. The resulting impregnated composite is thereafter heated to convert the compound employed to the corresponding oxide which, if desired, may be subsequently converted to the metal sulfide. If the catalyst contains the metal in elemental form, such as for example, metals of the platinum series, the silica-zirconia base, after treatment, with a water-soluble compound of such metal, may be subjected to treatment with hydrogen to effect reduction of the metal to its elemental form.

Suitable molybdenum compounds employed in the present process for impregnating the silica-zirconia base include ammonium molybdate, molybdenum tetrabromide, molybdenum oxydibromide, molybdenum tetrachloride, molybdenum oxydichloride, molybdenum oxypentachloride and molybdenum oxytetrafluoride. Suitable cobalt compounds include cobalt nitrate, cobalt ammine nitrate, cobalt ammine chloride, cobalt ammine sulfate, cobalt bromide, cobalt bromate, cobalt chloride, cobalt chlorate, cobalt fluoride, and cobalt fluorate.

In one method the particles of silica-zirconia base are initially subjected to a vacuum to remove air from the pores thereof and while maintaining the vacuum an impregnating solution such as described hereinabove is brought into contact with the particles of the silica-zirconia base. Alternatively, the silica-zirconia base may be impregnated with a solution of more than one compound, for example a solution of a molybdenum compound and a cobalt compound. Also, separate impregnating solutions of a molybdenum compound and a cobalt compound may be prepared and composited successively with the silica-zirconia base either with or without an intervening heating of the support. In general, using this technique, it is preferred to composite the molybdenum component first and then the cobalt component although the reverse procedure may be employed. After the impregnation, the base material is dried and calcined to convert the metal compounds to the oxides.

When utilizing a metal of the platinum series as the dehydrogenation component, one feasible method is to admix particles of the silica-zirconia base with an aqueous solution of an acid of the metal for example, chloroplatinic or chloropalladic acid or the ammonium salt of the acid of suitable concentration. It will be understood that any other suitable source of platinum metal may be used. Chloroplatinic acid generally is preferred because it is more readily available. Solutions of other feasible platinum-containing compounds include those of platinum ammine chlorides, trimethylbenzyl ammonium platinum chloride, tetra-amminoplatino chloride, platinum ammine nitrate, dinitrol diammino platinum and the like. The particles of silica-zirconia impregnated with a platinum metal compound is then dried and treated with hydrogen at elevated temperatures to reduce the platinum metal compound to the metal and to activate the catalyst.

It will be appreciated that in addition to the foregoing, other suitable water-soluble compounds of metals having hydrogenation-dehydrogenation activity either in the metallic form or in the form of an oxide or a sulfide may likewise be used. The particular amount of dehydrogenation component composited with the silica-zirconia base will vary depending upon the particular metal and the form in which such metal is employed. Thus, for composites containing a platinum metal, the amount of such metal contained in the catalyst will generally be between about 0.05 and about 10 percent by weight and, more particularly, between about 0.1 and about 5 percent by weight of the catalyst. The concentrations of the cobalt and molybdenum oxides in the catalyst described herein may respectively range from about 1 to about 10 percent by weight and from about 1 to about 20 percent by weight of the final catalyst. When chromia is employed as the dehydrogenation component, the content thereof will generally be in the approximate range of 2 to 20 percent by weight of the catalyst. When nickel is used, the metal content will be in the approximate range of 0.01 to 10 percent by weight of the catalyst. Tungsten, when used as the active dehydrogenation component, should be present in the approximate range of 1 to 20 percent by weight of the catalyst.

After impregnation, the composite generally is dried at a temperature of from about 200° F. to about 600° F. for a period of from about 2 to about 24 hours or more and thereafter calcined at a temperature of from about 600° F. to about 1300° F. for a period of from about 1 to 12 hours or more. As noted hereinabove, when a metal of the platinum series is employed as the dehydrogenation component, drying and calcination may be suitably carried out in a hydrogen atmosphere. In some instances, it is desirable to prepare the dehydrogenation component in the form of a metal sulfide. In such case, the composite after the above-described calcination, may be suitably treated in an atmosphere of hydrogen sulfide or a mixture of hydrogen sulfide and hydrogen at an elevated temperature such as for example about 800° F. In the case of tungsten sulfide or nickel tungsten sulfide, the tungsten may be deposited on the ammonium thiotungstate.

The hydrocracking process of this invention may be carried out in any suitable equipment for catalytic operations. The process may be operated batchwise. It is preferable, however, and generally more feasible to operate continuously. Accordingly, the process is adapted to operation using a fixed bed of catalyst. Also, the process can be operated using a moving bed of catalyst wherein the hydrocarbon flow may be concurrent or countercurrent to the catalyst flow. A fluid-type of operation wherein the catalyst is carried in suspension in the hydrocarbon charge may feasibly be employed using the present catalyst.

Hydrocracking, in accordance with the present process, is generally carried out at a temperature between about 600° F. and about 1050° F. and preferably between about 700° F. and about 900° F. The hydrogen partial pressure in such operation is generally within the range of about 100 and about 5000 pounds per square inch gauge and preferably about 1000 and 3000 pounds per square inch gauge. The liquid hourly space velocity of fresh feed, i.e. the liquid volume of hydrocarbons per hour per volume of catalyst is between about 0.1 and about 10 and preferably between about 0.25 and about 4. In general, the molar ratio of hydrogen to hydrocarbon charge employed, i.e. fresh feed is between about 2 and about 80 and preferably between about 5 and about 40.

Hydrocarbon charge stocks undergoing cracking in accordance with this invention comprise hydrocrackable hydrocarbons mixtures of such hydrocarbons and particularly hydrocarbon fractions having an initial boiling point of at least about 400° F., a 50 percent point of at least about 500° F. and an end boiling point of at least about 600° F. and boiling substantially continuously between said initial boiling point and said end boiling point. Such hydrocarbon fractions include gas oils, residual stocks, cycle stocks, whole topped crudes, and heavy hydrocarbon fractions obtained by the destructive hydrogenation of coal, tars, pitches, asphalts, and the like. As will be recognized the distillation of higher boiling petroleum fractions (about 750° F.) must be carried out under vacuum in order to avoid thermal cracking. The boiling temperatures utilized herein, however, are expressed for convenience in terms of the boiling point corrected to atmospheric pressure.

The hydrocracking selectivities of the catalysts described herein are evaluated by comparing their product distributions at fixed conversion levels. The conversion is defined as 100 minus the volume percent of charge remaining in the 650° F.+ boiling range. The products considered are dry gas (C_1–C_3), C_4 material, light naphtha (C_5—180° F.), heavy naphtha (180—390° F.), fuel oil (390–650° F.) and cycle stock (650° F.+). An overall measure of selectivity is the total yield of C_5—650° F. material at any conversion level since this range contains the more valuable products.

The hydrocracking activity of a catalyst as this term is utilized herein is defined as the temperature required to achieve a given conversion level.

The following examples will serve to illustrate the invention hereinabove described without limiting the same:

Examples 1 and 2 demonstrate the catalytic differences between two types of platinum silica-zirconia hydrocracking catalysts. The differences involve the method of preparing the silica-zirconia bases. In Example 1 the silica-zirconia base was formed above 6 pH and activated in hot acid while in Example 2 the silica-zirconia base was prepared by forming at 3.6 pH and activated in a steam atmosphere. The details of such examples are set forth below:

EXAMPLE 1

A catalyst of platinum on silica-zirconia was prepared by impregnating a silica-zirconia cogel containing 12.7 percent by weight ZrO_2 (on a dry solids basis), formed at 8.9–9.4 pH and activated in 1 percent by weight aqueous solution of H_2SO_4 for 24 hours at 175° F., with chloroplatinic acid to yield 0.9 percent by weight platinum on the finished catalyst.

The silica-zirconia base in this example was prepared in four batches by mixing, in each instance, 300 cc. of an aqueous solution of zirconium sulfate [$Zr(SO_4)_2 \cdot 4H_2O$] containing 0.05 g. ZrO_2/cc., 35 cc. of 50 percent by weight sulfuric acid diluted with 1470 cc. of water and 700 cc. of diluted N-Brand aqueous sodium silicate solution containing 0.193 g. SiO_2/cc. to yield a silica-zirconia hydrosol. The resulting sol set to a firm gel in 10–15 seconds having a pH of 8.9–9.4. This gel was cut into cubes and covered with a 1 weight percent aqueous solution of H_2SO_4 thus lowering the hydrogel pH to 1.7–2.0. Activation of the hydrogel was accomplished by heating in this solution for 24 hours at 175° F. The hydrogel was thereafter base-exchanged with a 2 weight percent aqueous ammonium chloride solution. The base-exchanged hydrogel was then water-washed free of chloride ion, dried for 16 hours at 280° F. in air and calcined 10 hours at 1200° F. in air. The silica-zirconia gel base so obtained was characterized by a pore volume of 0.46 cc./g.; an apparent density of 0.63 g./cc.; a surface area of 589 $m.^2/g.$ and a weight composition of 0.01 percent Na; 0.17 percent SO_4; 12.7 percent ZrO_2 and remainder SiO_2.

Platinum was deposited upon the silica-zirconia base by vacuum spray impregnating 107 grams of such base with 9.94 cc. of H_2PtCl_6 solution, containing 0.096 g. Pt/cc., diluted to 87.5 cc. with water. The resulting impregnated catalyst was wet aged 16 hours at 230° F. in a covered container so that very little loss of water occurred. The aged particles were thereafter reduced with hydrogen for 2 hours at 450° F. and 2 hours at 950° F. The finished catalyst had a density of 0.66 g./cc.; a surface area of 512 $m.^2/g.$ and contained 0.9 weight percent platinum and 0.19 weight percent chlorine.

EXAMPLE 2

The catalyst of this example was prepared by impregnating a silica-zirconia cogel containing 9.7 percent by weight ZrO_2 (on a dry solids basis), formed at 3.6 pH and activated in a non-drying steam atmosphere with chloroplatinic acid to yield 0.98 percent by weight platinum on the finished catalyst.

The silica-zirconia base was prepared by mixing 1200 cc. of aqueous zirconium sulfate solution containing 0.05 g. ZrO_2/cc., 248 cc. 50 percent by weight sulfuric acid, 5752 cc. of water and 2800 cc. of diluted N-Brand sodium silicate solution containing 0.193 g. SiO_2/cc. to yield a silica-zirconia hydrosol. The resulting hydrosol having a pH of 3.6 gelled in 4 to 5 hours at a room temperature of approximately 70–77° F. This hydrogel was then activated by subjecting to a non-drying steam atmosphere (200° F. wet bulb–220° F. dry bulb) for 2 hours. The hydrogel was thereafter dried at 240° F. and then base-exchanged with a 2 weight percent aqueous ammonium chloride solution. The base-exchanged hydrogel was then water-washed free of chloride ion, dried for 24 hours at 275° F. in air and calcined 10 hours at 1000° F. in air. The silica-zirconia gel base so obtained was characterized by a pore volume of 0.34 cc./g. and a weight composition of 0.03 percent Na; 0.07 percent SO_4; 9.7 percent ZrO_2 and remainder SiO_2.

Platinum was deposited upon the above silica-zirconia base in the same manner as in Example 1 to yield a resulting catalyst containing 0.98 weight percent platinum and 0.55 weight percent chlorine.

EXAMPLE 3

The base for the catalyst of this example was prepared by forming a silica-zirconia hydrosol by admixture of reactant solutions described in Example 2. The resulting sol having a pH of 3.6, formed a firm hydrogel in 4 to 5 hours at a room temperature of approximately 70–77° F. This hydrogel, after standing for 16 hours at the above room temperature, was cut into cubes and then activated by contacting with water for 24 hours at 175° F. The activated hydrogen was thereafter dried and processed in the same manner as in Example 2. The silica-zirconia gel base so obtained was characterized by a surface area of 490 $m.^2/g.$ and a weight composition of 0.06 percent Na; <0.09 percent SO_4; 11.0 percent ZrO_2 and remainder SiO_2.

Platinum was deposited upon the above silica-zirconia base in the same manner as in Example 1 to yield a catalyst containing 0.55 weight percent platinum and 0.17 weight percent chlorine.

The above catalysts of Examples 1, 2 and 3 were tested in hydrocracking a charge of 650° F. to tar West Texas gas oil. Hydrocracking was carried out at a 1 liquid hourly space velocity and at 2000 pounds per square inch gauge pressure, utilizing a hydrogen to hydrocarbon charge mol ratio of about 40 corresponding to 14,500 standard cubic feet of hydrogen per barrel of charge. Hydrogen and the charge stock were mixed together at the above pressure, heated to reaction temperature and passed downward through a bed of the catalyst contained

in the test unit. Hot effluent from the bottom of the catalyst bed was cooled and separated at the pressure utilized in the unit into gas and liquid product streams. The liquid product stream was stabilized at atmospheric pressure before being sampled for distribution and analysis. The gas recovered from the high pressure separation and from stabilizing the liquid product were sampled and analyzed. Activity of the catalysts was evaluated by operating the catalyst bed at a temperature level selected to convert 70 volume percent of the gas oil charge to material boiling below 650° F. The results of such testing are set forth in Table I hereinbelow. Referring to this table, the superiority of the catalyst of Example 1 over that of Example 2 and Example 3 is clearly evident from the 813° F. reactor temperature required for the 70 volume percent conversion, while the catalyst of Example 2 was so inactive and unstable that 70 percent conversion could not be achieved even at the maximum reactor temperature of 980° F. While the catalyst of Example 3 gave better results than that of Example 2, it likewise was so unstable that 70 volume percent conversion could not be achieved even at a reactor temperature of 901° F. Such data clearly demonstrate the advantages of high pH forming and low pH activation over low pH forming and activation of the hydrogel in water. Thus, the base prepared at low pH and activated with steam gave a very poor catalyst. The silica-zirconia base prepared at low pH and activated at such pH in water was active and unstable, while the base prepared at a pH in excess of 6 and activated at a low pH was both active and stable.

Examples 4, 5 and 6 illustrate the catalytic advantages of the catalyst utilizing the silica-zirconia gel prepared as described herein as the base for molybdena-silica-zirconia hydrocracking catalysts.

EXAMPLE 4

A silica-zirconia cogel was prepared by mixing the following reactants:

Solution A which consisted of 60 percent weight N-Brand sodium silicate and 40 percent weight water having a specific gravity of 1.206 at 80° F.

Solution B which consisted of acid-zirconium sulfate solution containing 6.61 percent weight $Zr(SO_4)_2 \cdot 4H_2O$, 89.77 percent weight H_2O, 3.62 percent weight H_2SO_4 and having a specific gravity of 1.064 at 80° F.

Solution A was continuously mixed in a nozzle at a rate of 380 cc./min. with 416 cc./min. of Solution B. The resulting silica-zirconia hydrosol having a pH of 8.2–8.5 set to a hydrogel in 2 seconds at 63° F. The sol was formed into spheroidal hydrogel beads by introducing globules of the sol into an oil medium. The resulting hydrogel beads were then treated 24 hours at 200° F. in 2 percent aqueous H_2SO_4 solution which reduced the hydrogen pH to 2.0. The acid-activated hydrogel was thereafter base-exchanged, washed and dried as in Example 1 and then calcined 20 hours at 1000° F. in air. The silica-zirconia gel base so obtained was charcterized by a pore volume of 0.44 cc./g.; an apparent density of 0.84 g./cc.; a surface area of 627 m.²/g. and a weight composition of 0.04 percent Na; 0.10 percent SO_4; 11.0 percent ZrO_2 and remainder SiO_2.

Molybdena was deposited upon the silica-zirconia base by vacuum spray impregnating 138 grams of such base in the form of 8/14 mesh size particles with 10 percent MoO_3 as a water solution of molybdic acid. This impregnated sample was then dried at 230° F. and calcined 3 hours at 1000° F. in air. The composite, so obtained, was sulfided with 50 percent H_2—50 percent H_2S mixture employing 2 volumes per volume of catalyst per minute for 5 hours at 800° F. The finished catalyst had a density of 0.71 g./cc., a surface area of 438 m.²/g. and contained 6.25 weight percent molybdenum and 2.91 weight percent sulfur.

EXAMPLE 5

A silica-zirconia base, containing 9.7 weight percent ZrO_2, was prepared as in Example 4 in the form of hydrogel beads. Such beads were then aged at room temperature for 2 hours followed by aging in 1 percent aqueous H_2SO_4 solution at 178–184° F. for 24 hours, resulting in a final pH of 2.4–4.2. The acid activated hydrogel was processed and calcined as in Example 4. The silica-zirconia gel base so obtained was characterized by a pore volume of 0.55 cc./g.; an apparent density of 0.60 g./cc.; a surface area of 523 m.²/g.; and a weight composition of 0.03 percent Na; 0.10 percent SO_4; 9.7 percent ZrO_2 and remainder SiO_2.

Molybdena was deposited upon the above silica-zirconia base in the same manner as employed in Example 4. The resulting composite had a density of 0.71 g./cc.; a surface area of 384 m.²/g. and contained 6.66 weight percent molybdenum. Prior to testing, the catalyst was treated with an equal volume mixture of hydrogen and hydrogen sulfide using the procedure employed in Example 4. After this treatment, the sulfur content of the catalyst was 4.31 percent by weight.

EXAMPLE 6

The silica-zirconia based used in preparing the catalyst of this example was made in a manner identical with that used in preparing the base of Example 2.

The silica-zirconia base so prepared was impregnated with MoO_3 as a water solution of molybdic acid in the same manner employed in Examples 4 and 5. The resulting catalyst had a surface area of 394 m.²/g. and a molybdenum content of 7.06 weight percent. Prior to testing the catalyst, it was treated with an equal volume mixture of hydrogen and hydrogen sulfide in the manner used in Examples 4 and 5. After this treatment, the sulfur content of the catalyst was 1.09 percent by weight.

The above catalysts of Examples 4, 5 and 6 were tested for hydrocracking using the charge stock and conditions described hereinabove in connection with the testing of the catalysts of Examples 1, 2 and 3. The results obtained are set forth in Table I hereinbelow. Comparing the properties of these catalysts, it will be seen that the catalysts of Examples 4 and 5 prepared from a hot acid activated silica-zirconia hydrogen are much superior in activity and selectivity to the catalyst of Example 6. Thus, reactor temperatures of 812 and 822° F. were respectively required in Examples 4 and 5 to hydrocrack the specified gas oil charge to produce 70 volume percent products boiling between 100 and 650° F. The catalyst of Example 6, on the other hand, at 950° F. gave only a 25 volume percent conversion to products boiling below 650° F.

The following example illustrates that an active and selective hydrocracking catalyst can be prepared using combined dehydrogenation components such as MoO_3 and CoO on a silica-zirconia base prepared in accordance with method described herein.

EXAMPLE 7

A silica-zirconia base containing approximately 11 percent by weight ZrO_2 was prepared by reacting 320 cc. of aqueous zirconium sulfate solution containing 0.05 g. ZrO_2/cc., 27 cc. of 50 percent by weight sulfuric acid, 1476 cc. of water and 700 cc. dilute N-Brand sodium silicate. The resulting silica-zirconia hydrosol set to a firm hydrogel in 30–50 seconds having a 6.3–6.8 pH. This gel was aged for 24 hours in water at room temperature, and then for 48 hours at 200° F. in ½ percent aqueous sulfuric acid solution reducing the pH of the hydrogel to 2.6. The hydrogel was thereafter base-exchanged, water washed and dried as in Example 1 and then calcined for 13 hours at 1000° F. in air. The silica-zirconia gel base so obtained was characterized by a pore volume of 0.54 cc./g.; an apparent density of 0.63 g./cc.; a surface area

of 597 m.²/g. and a weight composition of 0.01 percent Na, <0.01 percent So_4, 11.1 percent ZrO_2 and remainder SiO_2.

Hydrocracking catalyst was prepared by first vacuum spray impregnating the above silica-zirconia gel with 10 percent MoO_3 as a water solution of ammonium molybdate $[(NH_4)_6Mo_7O_{24}\cdot 4H_2O]$, drying at 220° F. for 16 hours and calcining 3 hours at 1000° F. in air. The resulting composite was then impregnated with 3 percent CoO as a water-solution of cobalt nitrate

$$[Co(NO_3)_2\cdot 6H_2O]$$

dried at 230° F. for 3 hours and calcined 10 hours at 1000° F. in air. The resulting catalyst was sulfided with a 50 percent H_2—50 percent H_2S mixture employing 2 volumes per volume of catalyst per minute for 5 hours at 800° F.

The resulting catalyst was tested as above and the results are shown in Table I hereinbelow. This catalyst, as will be evident from the results of such table showed good hydrocracking activity, requiring a reactor temperature of 823° F. to hydrocrack the gas oil charge to 70 volume percent of 100–650° F. products. The selectivity of this catalyst was also good showing 3.5 weight percent dry gas, 111.5 volume percent C_4+ products, heavy naphtha/fuel oil ratio of 0.76 and a fuel oil diesel index of 41.

Examples 8 and 9 respectively illustrate the preparation of hydrocracking catalysts of silica-zirconia base impregnated with the oxides of cobalt and molybdenum and with platinum wherein the base is characterized by a high diffusivity as a result of the inclusion of ground zircon sand in the initial hydrogel-forming reaction mixture.

EXAMPLE 8

A silica-zirconia cogel was prepared by mixing the following reactants:

Solution A which consisted of 54 percent weight N-Brand sodium silicate, 23 percent weight aqueous slurry containing 50 percent by weight of zircon sand having a weight mean particle diameter of <5 microns, and 23 percent weight water.

Solution B which consisted of acid-zirconium sulfate solution containing 6.6 percent weight $Zr(SO_4)_2\cdot 4H_2O$, 89.7 percent weight H_2O and 3.7 percent weight H_2SO_4.

Solution A was continuously mixed in a nozzle at a rate of 356 cc./min. with 386 cc./min. of Solution B. The resulting silica-zirconia hydrosol having a pH of 7.6–7.9 set to a hydrogel in 2–2.7 seconds, at 71° F. The sol was formed into spheroidal hydrogel beads by introducing globules of the sol into an oil medium. The resulting bead hydrogel containing, on a dry solids basis, 10 percent by weight cogelled zirconia while the 40 weight percent zircon powder contributing inert zirconia and produced a product of high diffusivity.

The resulting hydrogel beads were then aged for 20 hours at room itemperature in water and then for 24 hours at 200° F. in 1 percent aqueous H_2SO_4 solution resulting in a final hydrogel pH of 3.0. The hydrogel after such treatment was base-exchanged with 2 percent by weight aqueous ammonium chloride solution, water washed free of chloride ion, dried 16 hours at 270–280° F. in air and calcined 15 hours at 1000° F. in air. The silica-zirconia gel base so obtained was characterized by a pore volume of 0.40 cc./g.; an apparent density of 0.83 g./cc.; a surface area of 355 m.²/g. and a weight composition of 0.01 percent Na, <0.10 percent SO_4, 33.2 percent ZrO_2 and remainder SiO_2.

Molybdena was deposited on the silica-zirconia beads by vacuum spray impregnating with 10 percent MoO_3 as a water solution of molybdic acid, drying 16 hours at 230° F. and calcining 3 hours at 1000° F. in air. This calcined sample was then impregnated with 3 percent CoO as a water solution of cobalt nitrate, dried 16 hours at 230° F. followed by calcination in air at 1000° F. for 3 hours and sulfiding as in Example 4. The finished catalyst had a density of 0.99 g./cc., a surface area of 208 m.²/g. and contained 2.7 weight percent CoO, 5.59 weight percent molybdenum and 3.72 weight percent sulfur.

Hydrocracking 650° F. to tar West Texas gas oil with this catalyst at 2000 p.s.i.g., 1 LHSV: 14,500 s.c.f./bbl. H_2 circulation to 70 volume percent conversion required a reactor temperature of 855° F. At these conditions, the catalyst produced, as will be seen from Table I hereinbelow, 3.5 weight percent dry gas, 110.8 volume percent C_4+ product, consuming 1300 s.c.f./bbl. H_2. The heavy naphtha to fuel oil ratio was 0.72. The fuel oil had a diesel index of 40.

EXAMPLE 9

The silica-zirconia gel base used in preparing the catalyst of this example was made in the same manner as in Example 8 except the hydrogel was aged immediately in 1 percent aqueous H_2SO_4 solution. This hydrogel was then processed in the same manner as in Example 8. The silica-zirconia gel base so obtained was characterized by a pore volume of 0.44 cc./g.; an apparent density of 0.80 g./cc.; a surface area of 327 m.²/g. and a weight composition of 0.01 percent Na, <0.10 percent SO_4, 32.5 percent ZrO_2 and remainder SiO_2.

Platinum was deposited on 265 grams of the silica-zirconia gel base by vacuum spray impregnating with 0.51 percent Pt as an aqueous chloroplatinic acid solution made up of 14.81 cc. of H_2PtCl_6 containing 0.09 g. Pt/cc. diluted with water to a volume of 117 cc. The resulting impregnated sample was wet aged 16 hours at 230° F. in a covered container, followed by reduction with hydrogen for 2 hours at 450° F. and 2 hours at 950° F.

Hydrocracking with this catalyst using the charge stock and reaction conditions specified in previous examples required a reactor temperature of 835° F. At these conditions, the catalyst produced 3.5 weight percent dry gas while making 110.1 volume percent C_4+ product. The product heavy naphtha to fuel oil ratio was 0.79. The diesel index of the heavy naphtha was 49.

Examples 10 and 11 illustrate the preparation of active and selective hydrocracking catalysts wherein the particularly prepared silica-zirconia base is impregnated respectively with nickel-tungsten and nickel-molybdena.

EXAMPLE 10

The catalyst of this example was prepared by impregnating a silica-zirconia cogel base containing 89 weight percent SiO_2 and 11 weight percent ZrO_2 with 7.5 weight percent Ni and 13 weight percent W.

The silica-zirconia base was prepared by mixing dilute N-Brand sodium silicate with an acid-zirconium sulfate solution to yield a hydrosol having a pH of 8.2 which set to a firm hydrogel in 2–3 seconds. The resulting sol was formed into beads by introducing the sol in the form of globules into a water-immiscible oil wherein the globules set to hydrogel beads. The resulting hydrogel particles were aged in water for 4 hours at room temperature and thereafter in 2 weight percent aqueous sulfuric acid solution for 20 hours at 200° F. reducing the hydrogel pH to 2.3. The hydrogel, so activated, was then base-exchanged 8 times at two hour intervals with 2 weight percent aqueous ammonium sulfate solution, washed sulfate free with water and dried at 250–300° F.

The dried silica-alumina base was vacuum impregnated with an aqueous nickel nitrate solution to deposit 7.5 weight percent nickel, soaked 24 hours at room temperature, dried 16 hours at 240° F. and activated by calcining from 200° F. to 925° F. in air. The calcined composite, after cooling, was reimpregnated with 13 weight percent tungsten, employing an aqueous ammo-

nium tungstate solution. The product was then treated for 3 hours at 1000° F. with air flowing at a rate of 5 volumes per volume of product per minute and thereafter with an equal volume mixture of hydrogen and hydrogen sulfide for 5 hours at 800° F. utilizing 2 volumes of gaseous mixture per volume of product per minute. The treated product was cooled in nitrogen. The sulfur content of the finished catalyst was 6.5 weight percent.

EXAMPLE 11

The catalyst of this example was prepared using the same base as in Example 10 except that such base was calcined, prior to impregnation, for 3 hours at 1300° F. in air. The calcined base was then vacuum impregnated with aqueous nickel nitrate solution to deposit 6.2 weight percent nickel, dried for 24 hours at 240° F. and calcined for 3 hours at 1000° F. in air. The resulting composite was impregnated with 10 weight percent MoO_3, utilizing an aqueous solution of ammonium molybdate, dried for 24 hours at 240° F., and calcined 3 hours at 1000° F. in air. The resulting product was sulfided at 800° F. with an equal volume mixture of hydrogen and hydrogen sulfide in the same manner as in Example 10. The sulfur content of the finished catalyst was 5.5 percent by weight.

Catalytic evaluations of the above catalysts of Examples 10 and 11 with West Texas 650° F. to tar gas oil at 2000 p.s.i.g.; 1 LHSV; 14,500 s.c.f./bbl. H_2 are summarized in Table I. Referring to such data, it is seen that the dehydrogenation components of nickel-tungsten and nickel-molybdena in combination with the particularly prepared silica-zirconia base afforded active and selective hydrocracking catalysts. These catalysts required respectively 825° F. and 828° F. reactor temperature for 70 volume percent conversion of the gas oil charge to products boiling <650° F.

The following example illustrates the preparation of an active hydrocracking catalyst prepared by depositing nickel alone on the particularly prepared silica-zirconia base.

EXAMPLE 12

The catalyst of this example was prepared by impregnation of a silica-zirconia base formed at 8.3 pH, activated in a 2 weight percent aqueous sulfuric acid solution for 24 hours at 200° F. and thereafter processed in a manner similar to that described in Example 1. The activated silica-zirconia base (189.6 grams) was impregnated with 127 p.p.m. of nickel, employing 94 cc. of an aqueous solution of nickel nitrate. The impregnated product was dried for 16 hours at 230° F. and then calcined in air for 3 hours at 1000° F. The finished catalyst contained, on a dry basis, 127 p.p.m. of nickel and had a surface area of 613 $m.^2/g.$ and an apparent density of 0.72 g./cc.

The above catalyst was evaluated for hydrocracking activity by treating a Mid-Continent 650° F.+ gas oil at 2000 p.s.i.g.; 0.5 LHSV; 3000 s.c.f./bbl. H_2. The data obtained are summarized in Table I hereinbelow. Reference to such data show that the catalyst is capable of affording about 81.7 volume percent conversion of the charge with a good product distribution at 877° F. after 2.7 days on stream.

The above results, as well as those obtained upon testing the catalysts of Examples 1–11 for hydrocracking characteristics are shown below in Table I.

Table I

Example	1	2	3		4	5	6
Catalyst composition:							
CoO, percent weight							
Mo, weight percent					6.26	6.66	7.06.
Sulfur, percent weight					2.91	4.31	1.09.
Pt, percent weight	0.9	0.98	0.55				
Cl, percent weight	0.19	0.55	0.17				
Catalyst properties:							
Surface area, $m.^2/g$	512	375	403		438	384	394.
Density, g./cc	0.66		0.86		0.81	0.71	
Base description:							
Forming pH	8.9–9.4	3.6	3.6		8.5	8.5	3.6.
Activation:							
Room temp		24 hrs. H_2O	16 hrs.			2 hrs.	24 hrs. H_2O.
Solution	1% H_2SO_4	No.	H_2O		2% H_2SO_4	1% H_2SO_4	No.
Time, hrs.	24	2	24		24	24	2.
Temp., ° F.	175	200° wet bulb, 220° dry bulb.	175		200	178–184	200° wet bulb, 220° dry bulb.
Properties:							
Pore vol. cc./g	0.46				0.44	0.55	
App. dens., g./cc	0.63				0.85	0.60	
Surface area, $m.^2/g$	589		490		627	523	
Composition:							
Na, percent weight	0.01	0.03	0.06		0.04	0.03	
SO_4, percent weight	0.17	0.07	<0.09		0.10	<0.10	
ZrO_2, percent weight	12.7	9.7	11.0		11.0	9.73	
	Catalytic conversion of gas oil [1] (2,000 p.s.i.g., 1 LHSV, 14,500 SCF/bbl. H_2 circulation to 70 vol. percent (100–650° F. products))						
Reactor temp., ° F.	813	>980	[3] 813	[4] 901	812	822	950.
Dry gas, weight percent	2.5–3.0		6.5	6.5	3.5	3.2	
Total C_4's, vol. percent	4.0		12.2	11.5	8.0	5.2	
Total C_5's, vol. percent			12.2	10.4			
Light naphtha, vol. percent	4.3		6.3	7.9	6.0	4.3	
Heavy naphtha, vol. percent	31.5		22.9	15.5	25.0	28.2	
Lt. fuel oil, vol. percent	40.0				33.0	41.3	
Hvy. naph/fuel oil vol. percent	0.79				0.76	0.68	
C_4 plus product, vol. percent	113.3		111.1	107.8	110	112.2	
H_2 consumption, SCF/bbl.	1,425		1,622	1,210	1,100	1,400	
Product quality:							
Heavy Naph, 180–390° F.		[6]					[7].
Gr., API	50		53.2	52.5	49	50	
Lt. fuel oil, 390–650° F.:							
Gr., API	34–35				32.5	34	
Diesel index	50		55.1		39	43	
Sulfur, weight percent	0.01					0.01	
Heavy fuel oil:							
Gr., API	38				35.5	36.5	
Nitrogen, weight percent	0.01				0.001	0.001	
Sulfur, weight percent	0.05				0.02	0.01	

Table I—Continued

Example	7	8	9	10	11	12
Catalyst composition:						
CoO, percent weight	2.7	2.7		Ni 7.5	Ni 6.2	Ni 127 p.p.m.
Mo, weight percent	6.45	5.59		W 13	Mo 6.66	
Sulfur, percent weight	5.26	3.72		S 6.5	S 5.5	
Pt, percent weight			0.51			
Cl, percent weight			0.1			
Catalyst properties:						
Surface area, $m.^2/g$	471	208	315			613.
Density, g./cc	0.72	0.99	0.84			0.72.
Base description:						
Forming pH	6.3	7.6–7.9	7.6–7.9	8.2	→	8.3.
Activation:						
Room temp	24 hrs. H_2O	24 hrs. H_2O	1 hr. H_2O	4 hrs. at R.T		
Solution	½% H_2SO_4	1½ H_2SO_4	1% H_2SO_4	2% H_2SO_4	→	→
Time, hrs	48	24	24	20	→	24.
Temp., ° F	200	200	200	200	→	200.
Properties:						
Pore vol. cc./g	0.54	0.40	0.44	0.44	0.40	0.45.
App. dens., g./cc	0.63	0.83	0.80			0.73.
Surface area, $m.^2/g$	597	355	327	644	570	642.
Composition:						
Na, percent weight	0.01	0.01	0.01			<0.05.
SO_4, percent weight	<0.01	<0.10	<0.10			<0.09.
ZrO_2, percent weight	11.1	33.2	32.5	11.9	11.9	10.5.
	Catalytic conversion of gas oil [1] (2,000 p.s.i.g., 1 LHSV, 14,500 SCF/bbl. H_2 circulation to 70 vol. percent (100–650° F. products))					[2]
Reactor temp., ° F	823	855	835	825	828	877.[5]
Dry gas, weight percent	3.5	3.5	3.5	3.0	3.6	10.4.
Total C_4's, vol. percent	4.9	4.0	3.5	4.5	6.3	19.1.
Total C_5's, vol. percent				4.0	5.2	12.3.
Light naphtha, vol. percent	4.5	4.3	3.8	4.8	5.5	6.6.
Heavy naphtha, vol. percent	29.2	29.0	31.3	30.7	30.0	28.3.
Lt. fuel oil, vol. percent	39.0	40.0	39.8	38.3	34.6	23.0.
Hvy. naph/fuel oil vol. percent	0.76	0.72	0.79	0.81	0.87	1.23.
C_4 plus product, vol. percent	111.5	110.8	110.1	112.3	111.6	107.7.
H_2 consumption, SCF/bbl	1,410	1,300	1,425	1,470	1,350	1,342.
Product quality:						
Heavy Naph, 180–390° F						
Gr., API	50	50	50			
Lt. fuel oil, 390–650° F:						
Gr., API	33	33	35.5			
Diesel index	41	40	49			49.
Sulfur, weight percent	0.02					
Heavy fuel oil:						
Gr., API	36	35	35.5			
Nitrogen, weight percent	0.002					
Sulfur, weight percent	0.01					

[1] West Texas Gas Oil having a boiling range of 650° F. to 92.5% at 1,143° F.
[2] Mid-Continent 650° F. plus gas oil charge, 2,000 p.s.i.g., 0.5 LHSV, 3,000 SCF/bbl. H_2.
[3] 62 vol. percent conversion, 1.8 days on stream.
[4] 56.3 vol. percent conversion, 2.9 days on stream.
[5] 81.7 vol. percent conversion.
[6] Catalyst unstable—no balance run possible.
[7] 25% conversion; total product 26° API.

As will be seen from the above data, hydrocracking catalysts having a dehydrogenation component deposited on the silica-zirconia gel base prepared in the particular manner described herein are far more active, stable and selective in hydrocracking a heavy gas oil charge than catalysts produced using a silica-zirconia base prepared at conditions outside those specified in accordance with the present invention. Catalysts prepared in accordance with the method described herein are characterized by good activity and stability producing unexpectedly high yields of C_4+ products with little dry gas. The heavy naphtha to fuel oil ratios of the products formed established good gasoline production properties for the catalyst of the invention.

It will be understood that the above description is merely illustrative of preferred embodiments of the invention, of which many variations may be made by those skilled in the art without departing from the spirit thereof.

We claim:

1. A process for hydrocracking a hydrocarbon charge which comprises contacting the same in the presence of hydrogen at a temperature between about 600° F. and about 1050° F., at a liquid hourly space velocity between about 0.1 and about 10, a hydrogen partial pressure between about 100 and about 5000 pounds per square inch gauge employing a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80 with a catalyst composed of a dehydrogenation component deposited on a base consisting essentially of silica and zirconia having a zirconia content of between about 2 and about 20 percent by weight, prepared by reacting a water-soluble zirconium compound and an alkali metal silicate to effect formation of a gelable sol consisting essentially of silica and zirconia characterized by a pH in excess of 6 and a zirconia content, on a dry basis, of between about 2 and about 20, permitting said sol to set forming a silica-zirconia gel, reducing the pH of said gel to below 5 and maintaining the gel under such conditions of reduced pH while in contact with an aqueous medium at a temperature in the approximate range of 150 to 220° F. for a period of at least about 1 hour under conditions of substantially atmospheric pressure, thereafter washing the gel free of soluble matter, drying and calcining.

2. A process for hydrocracking a hydrocarbon charge which comprises contacting a hydrocarbon fraction having an initial boiling point of at least about 400° F., a 50 percent point of at least about 500° F. and an end point of at least about 600° F. and boiling substantially continuously between said initial boiling point and said end point in the presence of hydrogen at a temperature between about 600° F. and about 1050° F., at a liquid hourly space velocity between about 0.1 and about 10, a hydrogen partial pressure between about 100 and about 5000 pounds per square inch gauge employing a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80 with a catalyst composed of a dehydrogenation component deposited on a base consisting essentially of silica and zirconia having a zirconia content of between about 2 and about 20 percent by weight, prepared by reacting a water-soluble zirconium compound and an alkali metal silicate to effect formation of a gelable sol

consisting essentially of silica and zirconia characterized by a pH in excess of 6 and a zirconia content, on a dry basis, of between about 2 and about 20, permitting said sol to set forming a silica-zirconia gel, reducing the pH of said gel to below 5 and maintaining the gel under such conditions of reduced pH while in contact with an aqueous medium at a temperature in the approximate range of 150 to 220° F. for a period of at least about 1 hour under conditions of substantially atmospheric pressure, thereafter washing the gel free of soluble matter, drying and calcining.

3. A process for hydrocracking a hydrocarbon charge which comprises contacting the same in the presence of hydrogen at a temperature between about 600° F. and about 1050° F., at a liquid hourly space velocity between about 0.1 and about 10, a hydrogen partial pressure between about 100 and about 5000 pounds per square inch gauge, employing a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80 with a catalyst composed of a dehydrogenation component deposited on a base consisting essentially of silica and zirconia having a zirconia content of between about 2 and about 20 percent by weight, prepared by reacting a water-soluble zirconium compound and an alkali metal silicate having dispersed therein between about 2 percent and about 40 percent by weight of the dried base of a solid powdered material characterized by insolubility in the resulting hydrosol, infusibility at the temperature of calcination of the resulting base and a weight mean particle diameter of between about 1 and about 5 microns to effect formation of a gelable sol consisting essentially of silica and zirconia characterized by a pH in excess of 6 and a zirconia content, on a dry solids basis, of between about 2 and about 20 percent by weight, permitting the said sol to set forming a gel consisting essentially of silica and zirconia, reducing the pH of said gel to below 5 and maintaining the gel under such conditions of reduced pH while in contact with an aqueous medium at a temperature in the approximate range of 150 to 220° F. for a period of at least about 1 hour under conditions of substantially atmospheric pressure, thereafter washing the gel free of soluble matter, drying and calcining.

4. A process for hydrocracking a hydrocarbon charge which comprises contacting the same in the presence of hydrogen at a temperature between about 600° F. and about 1050° F., at a liquid hourly space velocity between about 0.1 and about 10, a hydrogen partial pressure between about 100 and about 5000 pounds per square inch gauge employing a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80 with a catalyst comprising a minor proportion of a dehydrogenation component selected from the group consisting of a metal, an oxide of a metal and a sulfide of a metal of groups V, VI and VIII of the periodic table deposited on a base consisting essentially of silica and zirconia having a zirconia content of between about 2 and about 20 percent by weight, prepared by reacting a water-soluble zirconium compound and an alkali metal silicate to effect formation of a gelable sol consisting essentially of silica and zirconia characterized by a pH in excess of 6 and a zirconia content, on a dry basis, of between about 2 and about 20, permitting said sol to set forming a silica-zirconia gel, reducing the pH of said gel to below 5 and maintaining the gel under such conditions of reduced pH while in contact with an aqueous medium at a temperature in the approximate range of 150 to 220° F. for a period of at least about 1 hour under conditions of substantially atmospheric pressure, thereafter washing the gel free of soluble matter, drying and calcining.

5. A process for hydrocracking a hydrocarbon charge which comprises contacting the same in the presence of hydrogen at a temperature between about 600° F. and about 1050° F., at a liquid hourly space velocity between about 0.1 and about 10, a hydrogen partial pressure between about 100 and about 5000 pounds per square inch gauge, employing a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80 with a catalyst comprising a minor proportion of molybdena deposited on a silica-zirconia base, said base having a zirconia content of between about 2 and about 20 percent by weight and prepared by reacting a water-soluble zirconium compound and an alkali metal silicate to effect formation of a gelable sol consisting essentially of silica and zirconia characterized by a pH in excess of 6 and a zirconia content, on a dry basis, of between about 2 and about 20, permitting said sol to set forming a silica-zirconia gel, reducing the pH of said gel to below 5 and maintaining the gel under such conditions of reduced pH while in contact with an aqueous medium at a temperature in the approximate range of 150 to 220° F. for a period of at least about 1 hour under conditions of substantially atmospheric pressure, thereafter washing the gel free of soluble matter, drying and calcining.

6. A process for hydrocracking a hydrocarbon charge which comprises contacting the same in the presence of hydrogen at a temperature between about 600° F. and about 1050° F., at a liquid hourly space velocity between about 0.1 and about 10, a hydrogen partial pressure between about 100 and about 5000 pounds per square inch gauge, employing a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80 with a catalyst comprising a minor proportion of nickel deposited on a silica-zirconia base, said base having a zirconia content of between about 2 and about 20 percent by weight and prepared by reacting a water-soluble zirconium compound and an alkali metal silicate to effect formation of a gelable sol consisting essentially of silica and zirconia characterized by a pH in excess of 6 and a zirconia content, on a dry basis, of between about 2 and about 20, permitting said sol to set forming a silica-zirconia gel, reducing the pH of said gel to below 5 and maintaining the gel under such conditions of reduced pH while in contact with an aqueous medium at at temperature in the approximate range of 150 to 220° F. for a period of at least about 1 hour under conditions of substantially atmospheric pressure, thereafter washing the gel free of soluble matter, drying and calcining.

7. A process for hydrocracking a hydrocarbon charge which comprises contacting the same in the presence of hydrogen at a temperature between about 600° F. and about 1050° F., at a liquid hourly space velocity between about 0.1 and about 10, a hydrogen partial pressure between about 100 and about 5000 pounds per square inch gauge, employing a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80 with a catalyst consisting essentially of a minor proportion of platinum deposited on a silica-zirconia base, said base having a zirconia content of between about 2 and about 20 percent by weight and prepared by reacting a water-soluble zirconium compound and an alkali metal silicate to effect formation of a gelable sol consisting essentially of silica and zirconia characterized by a pH in excess of 6 and a zirconia content, on a dry basis, of between about 2 and about 20, permitting said sol to set forming a silica-zirconia gel, reducing the pH of said gel to below 5 and maintaining the gel under such conditions of reduced pH while in contact with an aqueous medium at a temperature in the approximate range of 150 to 220° F. for a period of at least about 1 hour under conditions of substantially atmospheric pressure, thereafter washing the gel free of soluble matter, drying and calcining.

8. A process for hydrocracking a hydrocarbon charge which comprises contacting the same in the presence of hydrogen at a temperature between about 600° F. and about 1050° F., at a liquid hourly space velocity between about 0.1 and about 10, a hydrogen partial pressure between about 100 and about 5000 pounds per square inch gauge, employing a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80 with a catalyst consisting essentially of a minor proportion of

molybdenum oxide and cobalt oxide deposited on a silica-zirconia base, said base having a zirconia content of between about 2 and about 20 percent by weight and prepared by reacting a water-soluble zirconium compound and an alkali metal silicate to effect formation of a gelable sol consisting essentially of silica and zirconia characterized by a pH in excess of 6 and a zirconia content, on a dry basis, of between about 2 and about 20, permitting said sol to set forming a silica-zirconia gel, reducing the pH of said gel to below 5 and maintaining the gel under such conditions of reduced pH while in contact with an aqueous medium at a temperature in the approximate range of 150 to 220° F. for a period of at least about 1 hour under conditions of substantially atmospheric pressure, thereafter washing the gel free of soluble matter, drying and calcining.

9. A process for hydrocracking a hydrocarbon charge which comprises contacting the same in the presence of hydrogen at a temperature between about 600° F. and about 1050° F., at a liquid hourly space velocity between about 0.1 and about 10, a hydrogen partial pressure between about 100 and about 5000 pounds per square inch gauge, employing a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80 with a catalyst consisting essentially of a minor proportion of nickel and molybdenum oxide deposited on a silica-zirconia base, said base having a zirconia content of between about 2 and about 20 percent by weight and prepared by reacting a water-soluble zirconium compound and an alkali metal silicate to effect formation of a gelable sol consisting essentially of silica and zirconia characterized by a pH in excess of 6 and a zirconia content, on a dry basis, of between about 2 and about 20, permitting said sol to set forming a silica-zirconia gel, reducing the pH of said gel to below 5 and maintaining the gel under such conditions of reduced pH while in contact with an aqueous medium at a temperature in the approximate range of 150 to 220° F. for a period of at least about 1 hour under conditions of substantially atmospheric pressure, thereafter washing the gel free of soluble matter, drying and calcining.

10. A process for hydrocracking a hydrocarbon charge which comprises contacting the same in the presence of hydrogen at a temperature between about 600° F. and about 1050° F., at a liquid hourly space velocity between about 0.1 and about 10, a hydrogen partial pressure between about 100 and about 5000 pounds per square inch gauge, employing a molar ratio of hydrogen to hydrocarbon charge between about 2 and about 80 with a catalyst consisting essentially of a minor proportion of nickel and tungsten deposited on a silica-zirconia base, said base having a zirconia content of between about 2 and about 20 percent by weight and prepared by reacting a water-soluble zirconium compound and an alkali metal silicate to effect formation of a gelable sol consisting essentially of silica and zirconia characterized by a pH in excess of 6 and a zirconia content, on a dry basis, of between about 2 and about 20, permitting said sol to set forming a silica-zirconia gel, reducing the pH of said gel to below 5 and maintaining the gel under such conditions of reduced pH while in contact with an aqueous medium at a temperature in the approximate range of 150 to 220° F. for a period of at least about 1 hour under conditions of substantially atmospheric pressure, thereafter washing the gel free of soluble matter, drying and calcining.

11. A hydrocarbon conversion catalyst consisting essentially of a minor proportion of a dehydrogenation component selected from the group consisting of a metal, an oxide of a metal and a sulfide of a metal of groups V, VI and VIII of the periodic table deposited on a silica-zirconia base having a zirconia content of between about 2 and about 20 and prepared by reacting a water-soluble zirconium compound and an alkali metal silicate to effect formation of a gelable sol consisting essentially of silica and zirconia characterized by a pH in excess of 6 and a zirconia content, on a dry basis, of between about 2 and about 20, permitting said sol to set forming a silica-zirconia gel, reducing the pH of said gel to below 5 and maintaining the gel under such conditions of reduced pH while in contact with an aqueous medium at a temperature in the approximate range of 150 to 220° F. for a period of at least about 1 hour under conditions of substantially atmospheric pressure, thereafter washing the gel free of soluble matter, drying and calcining.

12. A hydrocarbon conversion catalyst consisting essentially of between about 2 and about 20 percent by weight of molybdena deposited on a silica-zirconia base having a zirconia content of between about 2 and about 20 and prepared by reacting a water-soluble zirconium compound and an alkali metal silicate to effect formation of a gelable sol consisting essentially of silica and zirconia characterized by a pH in excess of 6 and a zirconia content, on a dry basis, of between about 2 and about 20, permitting said sol to set forming a silica-zirconia gel, reducing the pH of said gel to below 5 and maintaining the gel under such conditions of reduced pH while in contact with an aqueous medium at a temperature in the approximate range of 150 to 220° F. for a period of at least about 1 hour under conditions of substantially atmospheric pressure, thereafter washing the gel free of soluble matter, drying and calcining.

13. A hydrocarbon conversion catalyst consisting essentially of between about 0.05 and about 10 percent by weight of platinum deposited on a silica-zirconia base having a zirconia content of between about 2 and about 20 and prepared by reacting a water-soluble zirconium compound and an alkali metal silicate to effect formation of a gelable sol consisting essentially of silica and zirconia characterized by a pH in excess of 6 and a zirconia content, on a dry basis, of between about 2 and about 20, permitting said sol to set forming a silica-zirconia gel, reducing the pH of said gel to below 5 and maintaining the gel under such conditions of reduced pH while in contact with an aqueous medium at a temperature in the approximate range of 150 to 220° F. for a period of at least about 1 hour under conditions of substantially atmospheric pressure, thereafter washing the gel free of soluble matter, drying and calcining.

14. A hydrocarbon conversion catalyst consisting essentially of between about 1 and about 10 percent by weight of cobalt oxide and between about 1 and about 20 percent by weight of molybdenum oxide deposited on a silica-zirconia base having a zirconia content of between about 2 and about 20 and prepared by reacting a water-soluble zirconium compound and an alkali metal silicate to effect formation of a gelable sol consisting essentially of silica and zirconia characterized by a pH in excess of 6 and a zirconia content, on a dry basis, of between about 2 and about 20, permitting said sol to set forming a silica-zirconia gel, reducing the pH of said gel to below 5 and maintaining the gel under such conditions of reduced pH while in contact with an aqueous medium at a temperature in the approximate range of 150 to 220° F. for a period of at least about 1 hour under conditions of substantially atmospheric pressure, thereafter washing the gel free of soluble matter, drying and calcining.

15. A hydrocarbon conversion catalyst consisting essentially of between about .01 and about 10 percent by weight of nickel and about 1 and about 20 percent by weight of molybdenum oxide deposited on a silica-zirconia base having a zirconia content of between about 2 and about 20 and prepared by reacting a water-soluble zirconium compound and an alkali metal silicate to effect formation of a gelable sol consisting essentially of silica and zirconia characterized by a pH in excess of 6 and a zirconia content, on a dry basis, of between about 2 and about 20, permitting said sol to set forming a silica-zirconia gel, reducing the pH of said gel to below 5 and maintaining the gel under such conditions of reduced pH

while in contact with an aqueous medium at a temperature in the approximate range of 150 to 220° F. for a period of at least about 1 hour under conditions of substantially atmospheric pressure, thereafter washing the gel free of soluble matter, drying and calcining.

16. A hydrocarbon conversion catalyst consisting essentially of between about .01 and about 10 percent by weight of nickel and about 1 and about 20 percent by weight of tungsten deposited on a silica-zirconia base having a zirconia content of between about 2 and about 20 and prepared by reacting a water-soluble zirconium compound and an alkali metal silicate to effect formation of a gelable sol consisting essentially of silica and zirconia characterized by a pH in excess of 6 and a zirconia content, on a dry basis, of between about 2 and about 20, permitting said sol to set forming a silica-zirconia gel, reducing the pH of said gel to below 5 and maintaining the gel under such conditions of reduced pH while in contact with an aqueous medium at a temperature in the approximate range of 150 to 220° F. for a period of at least about 1 hour under conditions of substantially atmospheric pressure, thereafter washing the gel free of soluble matter, drying and calcining.

17. A hydrocarbon conversion catalyst consisting essentially of a minor proportion of a dehydrogenation component selected from the group consisting of a metal, an oxide of a metal and a sulfide of a metal of groups V, VI and VIII of the periodic table deposited on a silicia-zirconia base having a zirconia content, of between about 2 and about 20 percent by weight and prepared by reacting a water-soluble zirconium compound and an alkali metal silicate having dispersed therein between about 2 and about 40 percent by weight of the dried base of a solid powdered material characterized by insolubility in the resulting hydrosol, infusibility at the temperature of calcination of the resulting base, and a weight mean particle diameter of between about 1 and about 5 microns to effect formation of a gelable sol comprising silica and zirconia characterized by a pH in excess of 6 and a zirconia content, on a dry basis, of between about 2 and about 20 percent by weight, permitting the said sol to set forming a gel consisting essentially of silica and zirconia, reducing the pH of said gel to below 5 and maintaining the gel under such conditions of reduced pH while in contact with an aqueous medium at a temperature in the approximate range of 150 to 220° F. for a period of at least about 1 hour under conditions of substantially atmospheric pressure, thereafter washing the gel free of soluble matter, drying and calcining.

18. A method for preparing a catalytic composite which comprises reacting in aqueous solution a water-soluble zirconium compound and an alkali metal silicate to effect formation of a gelable sol consisting essentially of silica and zirconia characterized by a pH in excess of 6 and a zirconia content, on a dry basis, of between about 2 and about 20, permitting said sol to set forming a silica-zirconia gel, reducing the pH of said gel to below 5 and maintaining the gel under such conditions of reduced pH while in contact with an aqueous medium at a temperature in the approximate range of 150 to 220° F. for a period of at least about 1 hour under conditions of substantially atmospheric pressure, washing the gel free of soluble matter, drying, calcining, and depositing on the resulting silica-zirconia gel a minor proportion of a dehydrogenation component selected from the group consisting of a metal, an oxide of a metal, and a sulfide of a metal of groups V, VI and VIII of the periodic table.

19. A method for preparing spheroidal particles of a hydrocracking catalyst which comprises reacting in aqueous solution, a water-soluble zirconium compound and an alkali metal silicate to effect formation of a gelable sol consisting essentially of silica and zirconia characterized by a pH in excess of 6 but not greater than 10, a gelation time of less than 20 seconds, and a zirconia content, on a dry basis, of between about 2 and about 20 percent by weight, introducing globules of the resulting hydrosol into a water-immiscible fluid wherein the globules of hydrosol set to spheroidal particles of hydrogel, effecting gelation of said spheroidal hydrosol particles, reducing the pH of said particles to below 5 but in excess of 1 and maintaining the hydrogel particles under such conditions of reduced pH while in contact with an aqueous acidic medium at a temperature in the approximate range of 175 to 220° F. for at least about 1 hour under conditions of substantially atmospheric pressure, water-washing the gel free of soluble matter, drying, calcining and depositing on the resulting spheroidal silica-zirconia gel a minor proportion of a dehydrogenation component selected from the group consisting of a metal, an oxide of a metal, and a sulfide of a metal of groups V, VI and VIII of the periodic table.

20. A method for preparing a catalytic composite which comprises reacting a water-soluble zirconium compound and an alkali metal silicate having dispersed therein between about 2 percent and about 40 percent by weight of the dried gel of a solid powdered material characterized by insolubility in the resulting hydrosol, infusibility at the temperature of calcination of the resulting gel and a weight mean particle diameter of between about 1 and about 5 microns to effect formation of a gelable sol consisting essentially of silica and zirconia characterized by a pH in excess of 6 and a zirconia content, on a dry basis, of between about 2 and about 20 percent by weight, permitting the said sol to set forming a gel comprising silica and zirconia, reducing the pH of said gel to below 5 and maintaining the gel under such conditions of reduced pH while in contact with an aqueous medium at a temperature in the approximate range of 150 to 220° F. for a period of at least about 1 hour under conditions of substantially atmospheric pressure, washing the gel free of soluble matter, drying, calcining, and depositing on the resulting silica-zirconia gel a minor proportion of a dehydrogenation component selected from the group consisting of a metal, an oxide of a metal, and a sulfide of a metal of groups V, VI and VIII of the periodic table.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,067,127 December 4, 1962

Charles J. Plank et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 42, for "usually" read -- unusually --; line 47, for "above-described desirable" read -- above-indicated desirable --; column 9, line 41, for "hot acid" read -- hot aqueous acid --; column 10, line 56, for "activated hydrogen" read -- activated hydrogel --; column 11, line 56, for "hydrogen" read -- hydrogel --; line 74, for "6.25" read -- 6.26 --; columns 17 and 18, Table I, third column, line 10 thereof, for "1½ H_2SO_4" read -- 1% H_2SO_4 --.

Signed and sealed this 21st day of May 1963.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents